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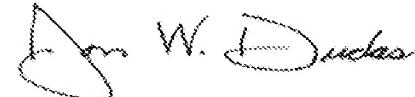
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APPLICATION NUMBER: 60/531,531

FILING DATE: *December 19, 2003*

RELATED PCT APPLICATION NUMBER: PCT/US04/42706

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WILSON
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December 19, 2003

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Patty Wilson

031356 U.S.PTO
60/531531



Mail Stop Provisional Application
Commissioner for Patents
P.O. Box 1450
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Re: U.S. Provisional Patent Application for
PHOTOCURABLE PERFLUOROPOLYETHERS FOR USE AS
NOVEL MATERIALS FOR CONTACT AND IMPRINT
LITHOGRAPHY
Our Ref. No. 421/90 PROV

Sir:

Please find enclosed the following:

1. Provisional Application Cover Sheet (1 pg.) in duplicate;
2. U.S. Provisional Patent Application (69 pgs.);
3. A return-receipt postcard to be returned to our offices with the U.S. Patent and Trademark Office date stamp thereon; and
4. A Certificate of Express Mail No.: EV412493405US.

Please contact our offices if there are any questions.

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Respectfully submitted,

JENKINS, WILSON & TAYLOR, P.A.



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This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. EV412493405US

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Joseph M. Jason	DeSimone Rolland	Durham, NC Durham, NC

Additional inventors are being named on the _____ separately numbered sheets attached hereto

TITLE OF THE INVENTION (500 characters max)

PHOTOCURABLE PERFLUOROPOLYETHERS FOR USE AS NOVEL MATERIALS FOR CONTACT AND IMPRINT LITHOGRAPHY

Direct all correspondence to:

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ENCLOSED APPLICATION PARTS (check all that apply)

- Specification Number of Pages **69**
- Drawing(s) Number of Sheets _____
- Application Data Sheet. See 37 CFR 1.76

CD(s), Number _____

Other (specify) _____

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- Applicant claims small entity status. See 37 CFR 1.27.
- A check or money order is enclosed to cover the filing fees.
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FILING FEE
Amount (\$)**160.00**

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

No.

Yes, the name of the U.S. Government agency and the Government contract number are: _____

[Page 1 of 1]

Respectfully submitted,

SIGNATURE Jeffrey L. WilsonTYPED or PRINTED NAME Jeffrey L. WilsonTELEPHONE 919-493-8000Date 12/19/03REGISTRATION NO. 36,058

(If appropriate)

Docket Number: 421/90 PROV

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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UNITED STATES PROVISIONAL PATENT APPLICATION

**PHOTOCURABLE PERFLUOROPOLYETHERS FOR USE AS NOVEL
MATERIALS FOR CONTACT AND IMPRINT LITHOGRAPHY**

Inventor: Joseph M. DeSimone, Ph.D.
Durham, North Carolina, USA

Jason Rolland
Durham, North Carolina, USA

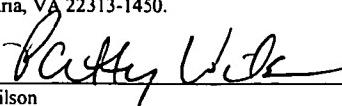
Assignee: The University of North Carolina at Chapel Hill

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Date of Deposit December 19, 2003

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Patty Wilson

PHOTOCURABLE PERFLUOROPOLYETHERS FOR USE AS NOVEL MATERIALS FOR CONTACT AND IMPRINT LITHOGRAPHY

STATEMENT OF THE INVENTION

5

The presently disclosed subject matter relates to photocurable perfluoropolyethers and their use in contact and print lithography. In some embodiments, the presently disclosed subject matter relates to the use of photocurable perfluoropolyethers for soft lithography. As used herein, the term "soft lithography" refers to a process by which micron and sub-micron features are transferred to a substrate through the use of elastomeric stamps. Soft lithography has emerged as an alternative to traditional photolithography processes for producing feature sizes smaller than about 100 nm. As used herein, the term "soft lithography" encompasses several processes including, but not limited to, imprint lithography, replica molding, microcontact printing, micromolding in capillaries, and solvent-assisted micromolding (SAMIM).

10

The elastomeric stamp is an important component of a soft lithography process. A poly(dimethyl siloxane) (PDMS) elastomer typically is used as the material for stamp fabrication. The presently disclosed subject matter addresses several problems inherent in the use of PDMS elastomers in soft lithography. First, PDMS elastomers swell in many organic solvents, such as hexanes, toluene, and dichloromethane. Such swelling can limit the polymers and solvents used in SAMIM techniques.

15

Second, the surface energy of PDMS elastomers often is not low enough to facilitate release in some soft lithography techniques known in the art. As a result, PDMS stamps must be functionalized with an O₂ plasma treatment followed by a fluorinated self-assembled monolayer (SAM) deposition to lower the surface energy of the PDMS material and allow for its release without damaging the resist features. The fluorination step also helps to prevent the

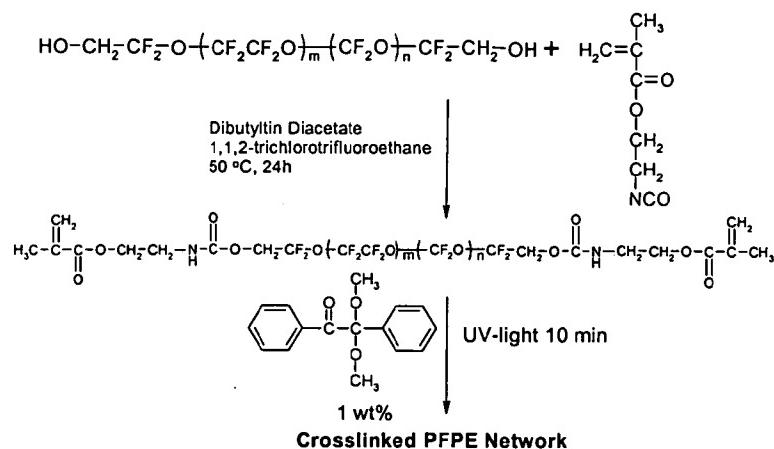
build up of residual resist that can occur on untreated PDMS stamps after repeated use. The build up of residual resist can destroy the features of the stamp and can ruin the stamp.

Third, the highly elastomeric behavior of PDMS, which is a consequence of the low modulus of typical PDMS elastomers, results in the deformation of the features on the stamp when it is subjected to stress. Finally, because PDMS elastomers are cured through a thermal platinum-catalyzed hydrosilation reaction at elevated temperatures, the material shrinks by a factor of about 1% upon curing. Such shrinkage is undesirable in sub-100 nm features.

The presently disclosed subject matter addresses the above-mentioned problems with PDMS elastomers by using a photocurable perfluoropolyether (PFPE) elastomer as a stamp in soft lithography. The PFPE elastomers of the presently disclosed subject matter comprise highly fluorinated functionalized PFPEs, which have liquid-like viscosities and can be cured into durable elastomers that exhibit the chemical resistance of typical fluoropolymers.

In some embodiments, the presently disclosed subject matter pertains to a method of synthesizing and photocuring a functional perfluoropolyether according to Scheme 1.

Scheme 1. Synthesis and Photocuring of Functional Perfluoropolyethers



In some embodiments of the presently disclosed subject matter, a PFPE elastomer is prepared which exhibits many desirable properties of PDMS

elastomers including, but not limited to, flexibility, ultraviolet (UV) transparency, and durability. In some embodiments of the presently disclosed subject matter, a PFPE elastomer is prepared which addresses many of the problems associated with the use of PDMS elastomers as stamps in soft lithography processes.

5 Accordingly, in some embodiments, a PFPE elastomer of the presently disclosed subject matter exhibits a low surface energy on the order of about 10×10^{-3} J m⁻², which is lower than that for PDMS-based materials. As a result, the fluorination step often required with PDMS stamps is not necessary to allow release of the PFPE elastomer without damaging the resist features. The build up of residual

10 resist after repeated use also is reduced in some embodiments of the presently disclosed subject matter.

In some embodiments of the presently disclosed subject matter, a PFPE elastomer is prepared which is resistant to organic solvents that cause swelling in PDMS elastomers. This feature allows new solvents and resist polymers to be

15 used in SAMIM techniques. A typical SAMIM technique employs a solvent that swells the organic polymer layer and wets the stamp, but does not swell it. The stamp is pressed to the organic polymer layer, which then swells to fill the features on the stamp. The solvent is allowed to evaporate and the stamp is peeled away leaving the desired pattern. Typical solvents used in SAMIM

20 techniques include aprotic solvents, such as acetone, and protic solvents, such as an alkyl alcohol. Most organic polymers, however, exhibit low solubility in acetone and alkyl alcohol solvents. The PFPE-elastomer stamps of the presently disclosed subject matter allow for the use of acetone and other aprotic solvents, such as tetrahydrofuran, dichloromethane, and toluene, which swell the organic

25 polymer layer without swelling the stamp.

In some embodiments of the presently disclosed subject matter, the modulus of a PFPE elastomer is regulated by incorporating monofunctional PFPEs into the network. This feature allows for the synthesis of rigid elastomers that are less susceptible to deformation when subjected to stress. Also, in some embodiments of the presently disclosed subject matter, the percentage of shrinkage, which is attributed to the use of elevated temperatures in the curing of

PDMS stamps, is reduced by the ability to photocure a PFPE material at room temperature.

The presently disclosed subject matter also can be used to fabricate solvent-compatible microfluidic devices, which are fabricated by using similar techniques to those used to generate stamps for soft lithography.

5

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THE UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL
REPORT OF INVENTION

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*We ask for "disclosing parties" rather than "inventors" because an inventor is one who contributes to the conception of an invention as that invention is subsequently defined by one or more patent claims; therefore the final determination on inventorship must wait until such time as a patent application is filed.

**If any of the inventors were employed by other institutions while the invention was being made, please include the name, address and phone number of that institution.

[FOR ADDITIONAL DISCLOSING PARTIES, PLEASE USE THE SAME FORMAT AS ABOVE AND ATTACH AS AN ADDENDUM AT THE END OF THIS REPORT]

Pursuant to the Patent Policy of The University of North Carolina at Chapel Hill, I/we hereby disclose details about the following invention:

a. TITLE OF INVENTION:

Photocurable Perfluoropolyethers for use as Novel Materials for Contact and Imprint Lithography

3. DATE OF INVENTION: [Indicate actual or approximate dates.]

Earliest conception*: 12-11-03
 Experimentation Period: 12-11-03 - present
 Reduction to Practice**: has not been reduced to practice

Are experimental data validating the invention or prototypes of the invention available?

Data has been collected on the synthesis, characterization, and photocuring of these perfluoropolyethers. We have also performed "soft lithography" techniques by which the materials are spin coated onto a patterned wafer, cured, and peeled from the wafer yielding a patterned stamp.

*Conception means the formation, in the mind of the inventor(s), of a definite and permanent idea of the complete and operative invention as claimed, as it is thereafter to be applied in practice.

**If the invention has not been reduced to practice, please so indicate.

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4. DESCRIPTION OF INVENTION:

Describe the invention in detail. Attach additional pages as necessary.

Soft lithography refers to the process by which micron and sub-micron features are transferred to a substrate through the use of elastomeric stamps. Soft lithography has emerged as a promising industrial alternative to traditional photolithography methods in producing feature sizes smaller than 100nm. There are many subdivisions of soft lithography which include (but are not limited to) imprint lithography (IL), replica molding (REM), microcontact printing (μ CP), micromolding in capillaries (MIMIC), and solvent-assisted micromolding (SAMIM). The most critical component of the soft lithography process is the elastomeric stamp. Traditionally many of the above listed techniques make use of poly(dimethyl siloxane) (PDMS) as the material for stamp fabrication. PDMS stamps offer some attractive qualities for soft lithography from a materials standpoint. It is an elastomer and can readily conform to a variety of structures. PDMS has a relatively low surface energy ($21.6 \times 10^{-3} \text{ J m}^{-2}$) which sometimes facilitates easy release from delicate molds. PDMS elastomers are UV transparent which is crucial for certain techniques such as imprint lithography and others.¹

Despite its advantages, the chemical and mechanical nature of PDMS elastomers impose limitations on its use in soft lithography. First, a major problem is that PDMS elastomers swell a great deal in many organic solvents such as hexanes, toluene, and dichloromethane. This factor can limit the polymers and solvents used in SAMIM which is illustrated in figure 2.

Second, while the surface energy of the material is low enough to facilitate release in some techniques, it is often not low enough. PDMS stamps are functionalized with an O₂ plasma treatment followed by a fluorinated SAM deposition. This step is necessary to further lower the surface energy of the material and allow for release without damaging the resist features. The fluorination step also helps prevent the build up of residual resist that occurs on untreated PDMS stamps after repeated use and can destroy the features as well as ruin the stamp^{1,2}.

Third, while the highly elastomeric behavior of PDMS is advantageous for reasons outlined above, it is also a large source of serious problems in stamping techniques. These problems result from the low modulus of PDMS elastomers such as Dow Corning's Sylgard 184 in which deformation of the features on the stamp occurs when it is subjected to stress^{1,2}.

Finally, because it is cured through a thermal platinum-catalyzed hydrosilation reaction the material shrinks by a factor of 1% upon curing. This can cause obvious problems with sub-100nm features.

As a solution to the above listed problems we propose the use of photocurable "Liquid Teflon" elastomers as stamps in soft lithography. The materials are highly fluorinated functionalized perfluoropolyethers (PFPEs) that have liquid-like viscosities and can be cured into tough, highly durable elastomers that exhibit the remarkable chemical resistance of fluoropolymers like Teflon™. The synthesis of these materials is shown in Scheme 1. We have recently proven the utility of these materials in the fabrication of solvent-compatible microfluidic devices. These devices are fabricated using similar techniques used to generate stamps for soft lithography. An example of this is shown in figure 1.

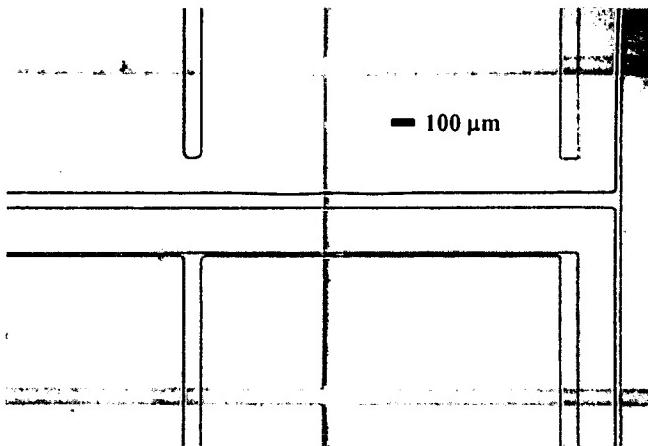
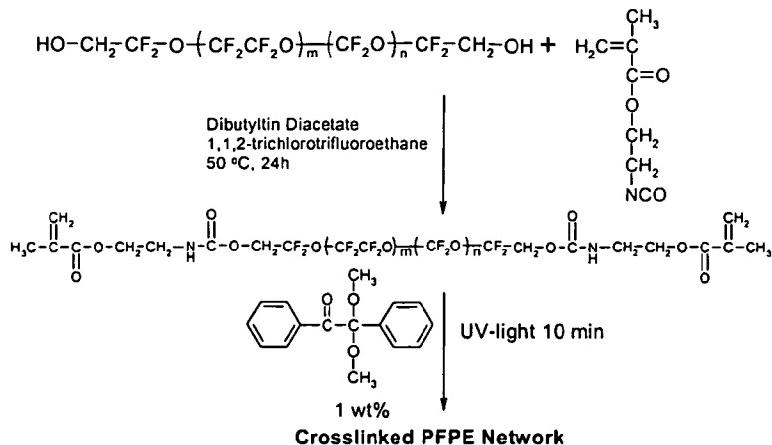


Figure 0. Patterned channels in a PFPE microfluidic device.

PFPE elastomers exhibit many of the desirable properties of PDMS elastomers including flexibility, UV transparency, and durability. In addition, these materials hold great promise to solve the problems with PDMS elastomers outlined above. Because they are highly fluorinated, the elastomers exhibit remarkably low surface energies on the order of $10 \times 10^{-3} \text{ J m}^{-2}$ which is significantly lower than PDMS-based materials. Thus, the fluorination step often employed with PDMS stamps would be unnecessary to allow release without damage to the resist features. Buildup of residual resist after repeated use would also be greatly reduced if not eliminated.

Second, the elastomers have proven to be remarkably resistant to organic solvents that greatly swell PDMS elastomers. This would allow for SAMIM techniques outline in figure 2 to be expanded to new solvents and resist polymers. The technique uses a solvent that swells the organic polymer layer and wets the PDMS stamp but does not swell it. The stamp is pressed to the organic polymer layer which then swells to fill the features on the stamp. Following this, the solvent is allowed to evaporate and the stamp is peeled away leaving the desired pattern. Solvents employed for this technique include acetone and alkyl alcohols such as methanol and ethanol¹. However, most organic polymers exhibit greatly limited solubility in these solvents. Our PFPE-elastomer stamps would allow the use of solvents such as tetrahydrafuran, dichloromethane, and toluene that greatly swell organic polymers without swelling the stamp.

Scheme 0. Synthesis and Photocuring of functional perfluoropolyethers



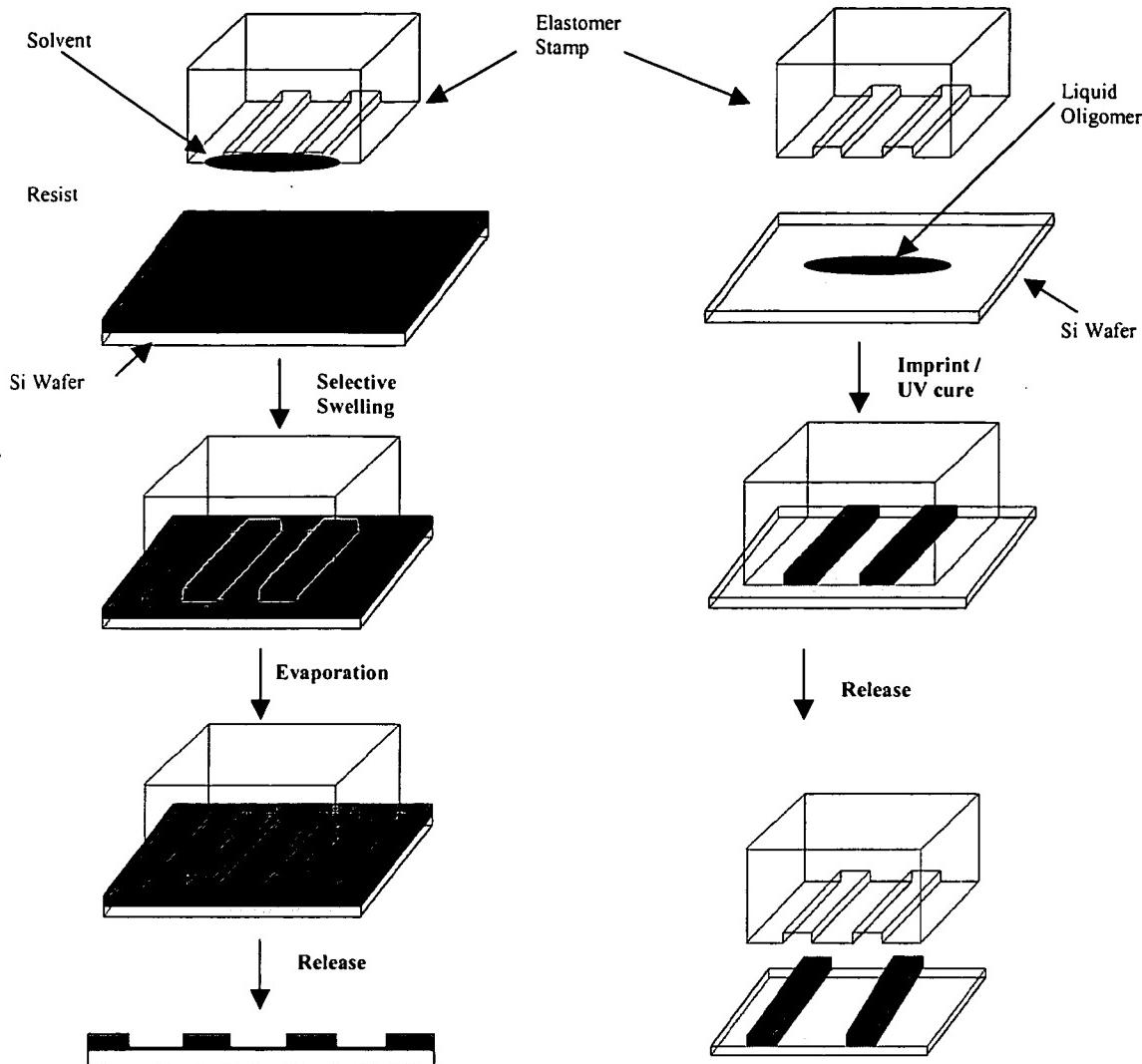
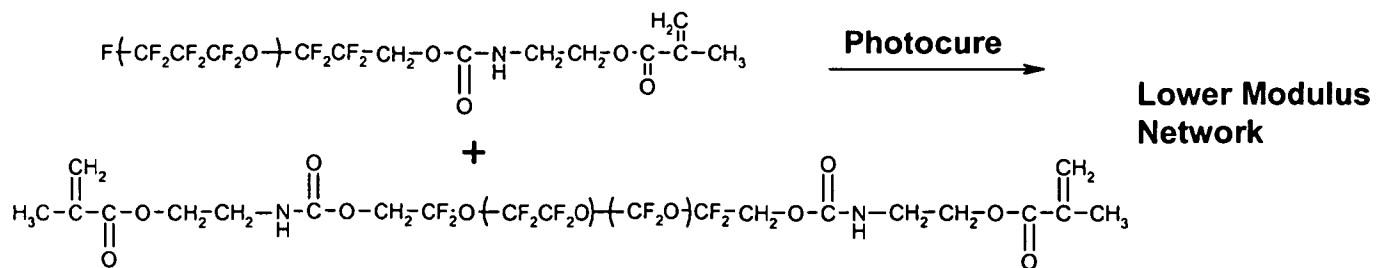


Figure 0. Schematic illustrations of SAMIM and IL soft lithography

Thirdly, we possess the ability to easily tune the modulus of these "Liquid Teflon" based elastomers by incorporating monofunctional PFPEs into the network (scheme 2). This will allow the synthesis of more rigid elastomers that should be less susceptible to deformation when subjected to a stress. Also the ability to photocure of our materials at room temperature should reduce the % shrinkage which has been attributed to the elevated temperatures used in the curing of PDMS stamps.

Scheme 0. Synthesis of PFPE elastomers with "tunable" modulus.



References:

- 1) Whitesides, G. M.; Younan, X. *Angew. Chem. Int. Ed.* **1998**, *37*, 550-575
- 2) Resnick, D. J.; Mancini, D. P.; Sreenivasan, S. V.; Willson, C.G. *Semiconductor International* **2002**, June, 71.

- a. Write a brief descriptive abstract of the invention without disclosing any confidential information. This may be used for marketing purposes.

The invention described involves the usage of novel functionalized "Liquid Teflon" PFPE materials in the fabrication of stamps used for a variety of soft lithography techniques. These advanced materials will allow for the fabrication of stamps that will greatly improve soft lithography thus allowing for rapid fabrication of sub 100 nm features without the use of conventional photolithography. They specifically offer huge advantages over PDMS stamps especially in solvent assisted micromolding (SAMIM) and Imprint lithography (IL) techniques.

- b. Expand on novel and unusual features which distinguish this invention from present technology. What problems does the invention solve or what advantages does it possess?

Our photocurable "Liquid Teflon" materials offer several advantages over current PDMS stamps:

- 1) They offer a much lower surface energy which allows for easy mold release without the plasma treatment and fluorination steps used for PDMS stamps. This also aids in the prevention of "fouling" from residual polymer resist material that is found to build up on PDMS devices after multiple uses.
 - 2) They offer remarkable resistance to swelling in organic solvents. The swelling of PDMS-based stamps has greatly restricted the SAMIM technique to using alkyl alcohols or acetone as solvents. This is a problem because these solvents do not swell most organic polymers. With our materials solvents such as tetrahydrofuran, toluene and methylene chloride which greatly swell organic polymers are able to be used. This could also allow the IL technique to expand to using viscous polymer solutions rather than viscous oligomers.
 - 3) They offer a tunable modulus that will result in a much stiffer elastomer. This has been a problem for current PDMS materials because the submicron size features are distorted when a stress is put on the stamp.
 - 4) They can be photocured at room temperature. This allows rapid fabrication of stamps as well as reduced % shrinkage after curing which is problematic with PDMS elastomers that are cured at elevated temperatures.
- c. Comment on possible uses for the invention. In addition to immediate applications, are there other uses that might be realized in the future?

In recent article in Semiconductor International, the limitations of traditional photolithography methods are outlined. It has been predicted that sub 100 nm features will need to resort to novel methods which include a variety of soft lithography techniques. The current material of choice for these soft lithography

techniques has been PDMS elastomers. While some success has been achieved, the material is limited for several reasons : It greatly swells in common organic solvents, it has a low modulus which facilitates the distortion of features when a stress is applied, its surface energy is not low enough for several soft lithography techniques and surface fluorination steps must be employed, it shrinks upon curing because it is cured at elevated temperatures. Our materials solve these problems and thus could allow the regular production of integrated circuits with sub 100 nm features.

- d. Describe any disadvantages or limitations of the invention. Can they be overcome? How?

The only disadvantage of the use of PFPE materials is the cost. PFPEs are much more expensive than PDMS materials. However, soft lithography utilizes only minute quantities of the polymer, thus the cost of these materials is virtually a non-issue.

- e. Are there known inventions or products that would compete with this one? Please describe, including information on relevant patents and publications, if available.

As described previously, the PDMS prepolymers, commercially known as Sylgard 184 are the current materials of choice for soft lithography.

- g. Are there any prior patent applications or patents by the inventor(s) related to this invention? If so, list the serial number(s) and filing date(s).

[USE ADDITIONAL SHEETS IF NECESSARY AND ATTACH DESCRIPTIVE MATERIALS
THAT MAY PROMOTE A BETTER UNDERSTANDING OF THE INVENTION]

OTD _____ - _____

C O N F I D E N T I A L

5. PREVIOUS AND/OR FUTURE DISCLOSURES OF THE INVENTION:

- a. Indicate details of any full or partial prior disclosure of this invention such as: manuscript, article, report, grant application, thesis, abstract, poster, demonstration, sales catalog, news release, internal memorandum, oral presentation, or discussion with an industry representative. SPECIFY DATE AND ATTACH COPIES OF ANY WRITTEN DISCLOSURE.

There has been no disclosure of the above invention.

- b. Have there been any changes in the invention since publication? If so, describe.

- c. Describe in detail any plans for future disclosure of this invention. This may include submission of a manuscript, article, report, grant application, thesis, abstract, poster, demonstration, sales catalog, news release, internal memorandum, oral presentation, or discussion with an industry representative, offer of samples, or a sale. **SPECIFY DATE AND ATTACH COPIES OF PROPOSED WRITTEN DISCLOSURE.**

Future disclosure of the above invention will likely be through patents, manuscripts, thesis, and oral presentations.

- d. Describe any other factors that might influence the decision whether or not and when to file a patent application, e.g., past or future public use of the invention, disclosure, or the likelihood that similar technology may be developed elsewhere.

6. SPONSORSHIP FOR WORK LEADING TO THE INVENTION: (this includes industry, foundation and state or federal sponsorship. If there is no sponsorship, type "none" in the sponsor field.)

- a. Name of sponsor(s): _____
 Complete sponsor contract/grant number(s): _____ UNC-CH Acct. Number: _____
 Funding period:
 Principal Investigator(s): _____
- b. Please list **any** encumbrances or obligations affecting this invention due to a Material Transfer Agreement, receipt of equipment or supplies, or other obligations.

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7. PROSPECTS FOR COMMERCIALIZATION:

- a. Indicate any apparent commercial interest. Please name companies and specific persons if possible.
- b. List names of other qualified firms that make comparable equipment or products, with your comments, if any.

Dow Corning – Manufacturers of Sylgard 184

8. CONFLICT OF INTEREST INFORMATION: (use extra sheets as needed)

- a. Do any of the disclosing parties serve as either a director, officer, or board member

of the company or companies named in 6 or 7 above? If so, please list in what capacity each person serves.

- b. Do any of the disclosing parties consult for any of these companies? If so, please list the company(ies) for which each consults.
- c. Do any of the disclosing parties hold a financial interest in any of the companies? If so, please list the company(ies) in which financial interest is held.

[Use the space below and additional sheets to elaborate on answers to questions and to provide any other helpful information.]

OTD _____ - _____

CONFIDENTIAL**Signature(s) of Disclosing Party(ies):**

_____	date _____

Signature of Person Witnessing This Disclosure: [This should be a non-discloser with the technical expertise to understand the invention.]

The undersigned has read and understands this Report of Invention:

_____	Signature	date
_____	Typed name and title	

Signature of Department Chairperson(s) Affected by this Disclosure*:

_____	Signature	date	_____	Signature	date
_____	Typed name and title		_____	Typed name and title	
_____	Signature	date	_____	Signature	date
_____	Typed name and title		_____	Typed name and title	

* By signing in the appropriate space, the Department Chairperson(s) is indicating only that he/she has seen and reviewed this Report of Invention.

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Office of Technology Development:

_____	Signature	Date disclosure received by Office of Technology Development
_____	Typed name and title	

Soft Lithography Using Photocurable “Liquid Teflon” Elastomeric Stamps

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Soft lithography refers to the process by which micron and sub-micron features are transferred to a substrate through the use of elastomeric stamps. Soft lithography has emerged as a promising industrial alternative to traditional photolithography methods in producing feature sizes smaller than 100nm. There are many subdivisions of soft lithography which include (but are not limited to) imprint lithography (IL), replica molding (REM), microcontact printing (μ CP), micromolding in capillaries (MIMIC), and solvent-assisted micromolding (SAMIM). The most critical component of the soft lithography process is the elastomeric stamp. Traditionally many of the above listed techniques make use of poly(dimethyl siloxane) (PDMS) as the material for stamp fabrication. PDMS stamps offer some attractive qualities for soft lithography from a materials standpoint. It is an elastomer and can readily conform to a variety of structures. PDMS has a relatively low surface energy ($21.6 \times 10^{-3} \text{ J m}^{-2}$) which sometimes facilitates easy release from delicate molds. PDMS elastomers are UV transparent which is crucial for certain techniques such as imprint lithography and others.¹

Despite its advantages, the chemical and mechanical nature of PDMS elastomers impose limitations on its use in soft lithography. First, a major problem is that PDMS elastomers swell a great deal in many organic solvents such as hexanes, toluene, and dichloromethane. This factor can limit the polymers and solvents used in SAMIM which is illustrated in figure 2.

Second, while the surface energy of the material is low enough to facilitate release in some techniques, it is often not low enough. PDMS stamps are functionalized with an O₂ plasma treatment followed by a fluorinated SAM deposition. This step is necessary to further lower the surface energy of the material and allow for release without damaging the resist features. The fluorination step also helps prevent the build up of residual resist that occurs on untreated PDMS stamps after repeated use and can destroy the features as well as ruin the stamp^{1,2}.

Third, while the highly elastomeric behavior of PDMS is advantageous for reasons outlined above, it is also a large source of serious problems in stamping techniques. These problems result from the low modulus of PDMS elastomers such as Dow Corning’s Sylgard 184 in which deformation of the features on the stamp occurs when it is subjected to stress^{1,2}.

Finally, because it is cured through a thermal platinum-catalyzed hydrosilation reaction the material shrinks by a factor of 1% upon curing. This can cause obvious problems with sub-100nm features.

As a solution to the above listed problems we propose the use of photocurable “Liquid Teflon” elastomers as stamps in soft lithography. The materials are highly fluorinated functionalized perfluoropolyethers (PFPEs) that have liquid-like viscosities

and can be cured into tough, highly durable elastomers that exhibit the remarkable chemical resistance of fluoropolymers like TeflonTM. The synthesis of these materials is shown in Scheme 1. We have recently proven the utility of these materials in the fabrication of solvent-compatible microfluidic devices. These devices are fabricated using similar techniques used to generate stamps for soft lithography. An example of this is shown in figure 1.

Scheme 0. Synthesis and Photocuring of functional perfluoropolyethers

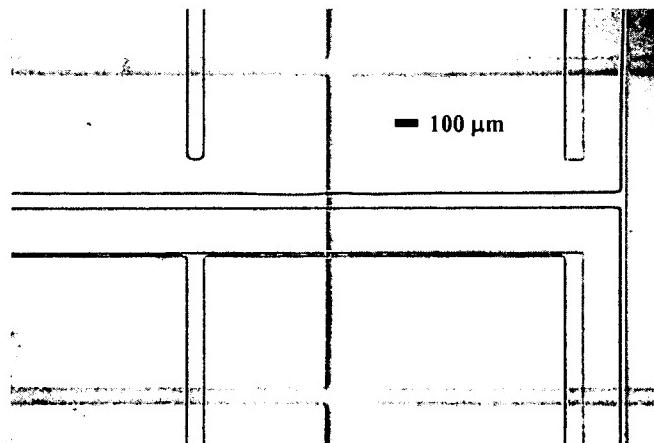
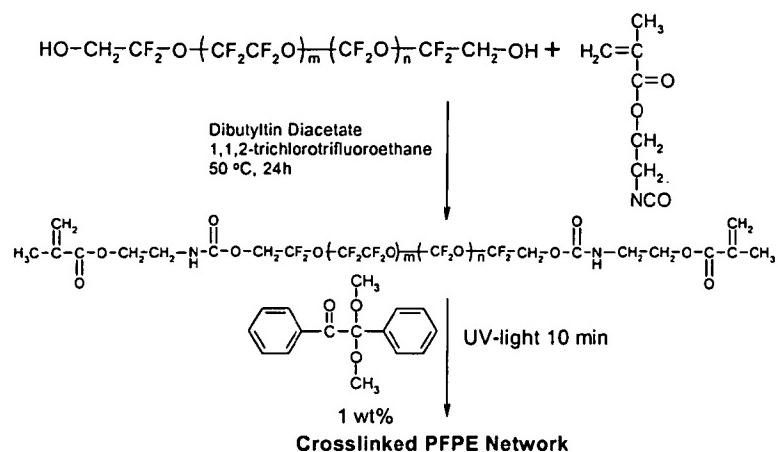


Figure 0. Patterned channels in a PFPE microfluidic device.

PFPE elastomers exhibit many of the desirable properties of PDMS elastomers including flexibility, UV transparency, and durability. In addition, these materials hold great promise to solve the problems with PDMS elastomers outlined above. Because they are highly fluorinated, the elastomers exhibit remarkably low surface energies on the order of $10 \times 10^{-3} \text{ J m}^{-2}$ which is significantly lower than PDMS-based materials. Thus, the fluorination step often employed with PDMS stamps would be unnecessary to allow release without damage to the resist features. Buildup of residual resist after repeated use would also be greatly reduced if not eliminated.

Second, the elastomers have proven to be remarkably resistant to organic solvents that greatly swell PDMS elastomers. This would allow for SAMIM techniques outline in figure 2 to be expanded to new solvents and resist polymers. The technique uses a solvent that swells the organic polymer layer and wets the PDMS stamp but does not swell it. The stamp is pressed to the organic polymer layer which then swells to fill the features on the stamp. Following this, the solvent is allowed to evaporate and the stamp is peeled away leaving the desired pattern. Solvents employed for this technique include acetone and alkyl alcohols such as methanol and ethanol¹. However, most organic polymers exhibit greatly limited solubility in these solvents. Our PFPE-elastomer stamps would allow the use of solvents such as tetrahydrafuran, dichloromethane, and toluene that greatly swell organic polymers without swelling the stamp.

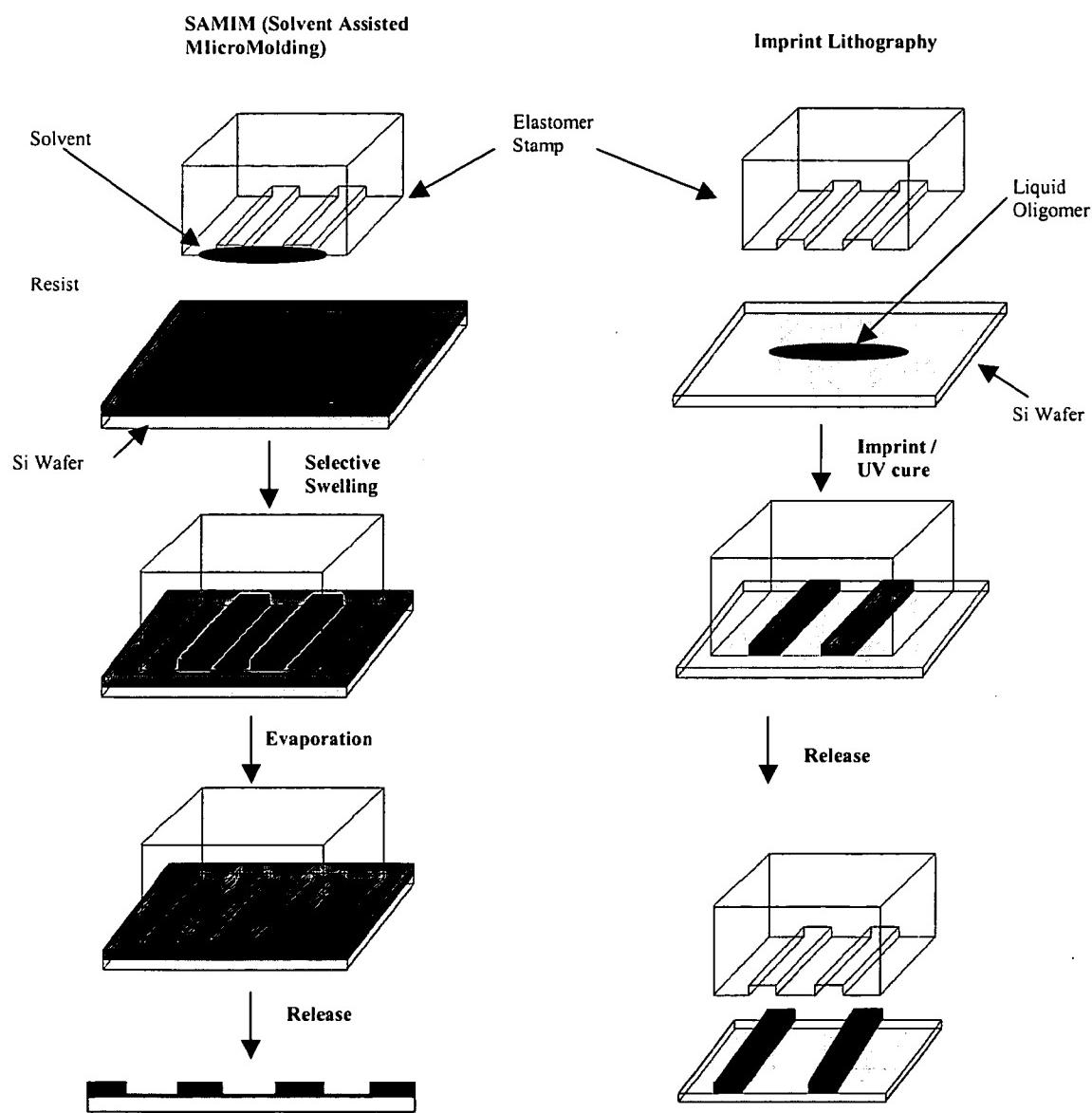
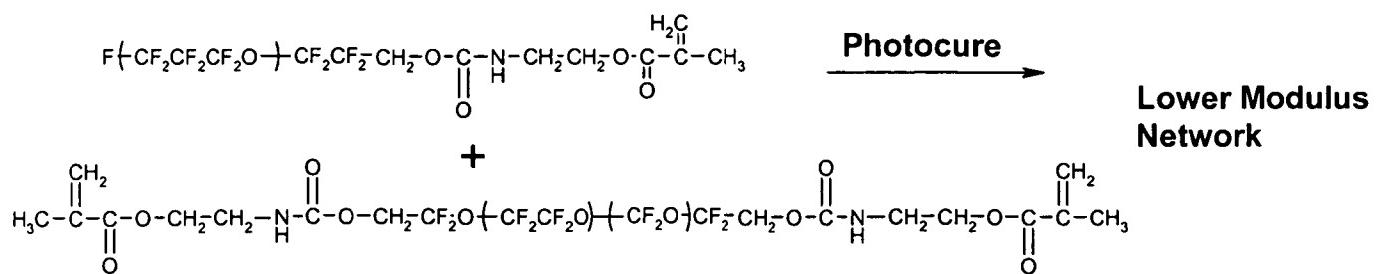


Figure 0. Schematic illustrations of SAMIM and IL soft lithography

Thirdly, we possess the ability to easily tune the modulus of these "Liquid Teflon" based elastomers by incorporating monofunctional PFPEs into the network (scheme 2). This will allow the synthesis of more rigid elastomers that should be less susceptible to deformation when subjected to a stress. Also the ability to photocure of our materials at room temperature should reduce the % shrinkage which has been attributed to the elevated temperatures used in the curing of PDMS stamps.

Scheme 0. Synthesis of PFPE elastomers with "tunable" modulus.



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Deposition with a polyimide mold provides this patterned microstructure.

ANGEWANDTE
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100 μm

Soft Lithography

Younan Xia and George M. Whitesides*

Microfabrication, the generation of small structures, is essential to much of modern science and technology; it supports information technology and permeates society through its role in microelectronics and optoelectronics. The patterning required in microfabrication is usually carried out with photolithography. Although it is difficult to find another technology with more dominant influence, photolithography nonetheless has disadvantages. The sizes of the features it can produce are limited by optical diffraction, and the high-energy radiation needed for small features requires complex facilities and technologies. Photolithography is expensive; it cannot be easily

applied to nonplanar surfaces; it tolerates little variation in the materials that can be used; and it provides almost no control over the chemistry of patterned surfaces, especially when complex organic functional groups of the sorts needed in chemistry, biochemistry, and biology are involved. We wished to develop alternative, non-photolithographic microfabrication methods that would complement photolithography. These techniques would ideally circumvent the diffraction limits of photolithography, provide access to three-dimensional structures, tolerate a wide range of materials and surface chemistries, and be inexpensive, experimentally convenient, and accessible to

molecular scientists. We have developed a set of such methods that we call "soft lithography", since all members share the common feature that they use a patterned elastomer as the mask, stamp, or mold. We describe here soft lithography, and survey its ability to provide routes to high-quality patterns and structures with lateral dimensions of about 30 nm to 500 μm in systems presenting problems in topology, materials, or molecular-level definition that cannot (or at least not easily) be solved by photolithography.

Keywords: elastomers • materials science • patterning • supramolecular chemistry

1. Introduction

The ability to generate small structures is central to modern science and technology. There are many opportunities that might be realized by making new types of small structures, or by downsizing existing structures.^[1] The most obvious examples are in microelectronics, where "smaller" has meant better—less expensive, more components per chip, faster operation, higher performance, and lower power consumption—since the invention of transistors in 1947.^[2] It is also clear that many interesting new phenomena occur at nanometer dimensions: Examples include electronic processes such as quantum size effect (QSE),^[3] Coulomb blockade,^[4] and single-electron tunneling (SET).^[4]

Microfabrication has its foundations in microelectronics, and it will continue to be the basis for microprocessors, memories, and other microelectronic devices for information technology in the foreseeable future. It is also increasingly

being applied in areas outside of microelectronics (Figure 1).^[5–9] Miniaturization and integration of a range of devices have resulted in portability; reductions in time, cost, reagents, sample size, and power consumption; improvements in detection limits; and new types of functions.

Photolithography is the most successful technology in microfabrication.^[10] It has been the workhorse of semiconductor industry since its invention in 1959: Essentially all integrated circuits are made by this technology. The photolithographic techniques currently used for manufacturing microelectronic structures are based on a projection-printing system (usually called a stepper) in which the image of a reticle is reduced and projected onto a thin film of photoresist that is spin-coated on a wafer through a high numerical aperture lens system. The resolution R of the stepper is subject to the limitations set by optical diffraction according to the Rayleigh Equation (1),^[10a] where λ is the wavelength of

$$R = k_1 \lambda / \text{NA} \quad (1)$$

the illuminating light, NA the numerical aperture of the lens system, and k_1 a constant that depends on the photoresist. Although the theoretical limit set by optical diffraction is usually about $\lambda/2$, the minimum feature size that can be ob-

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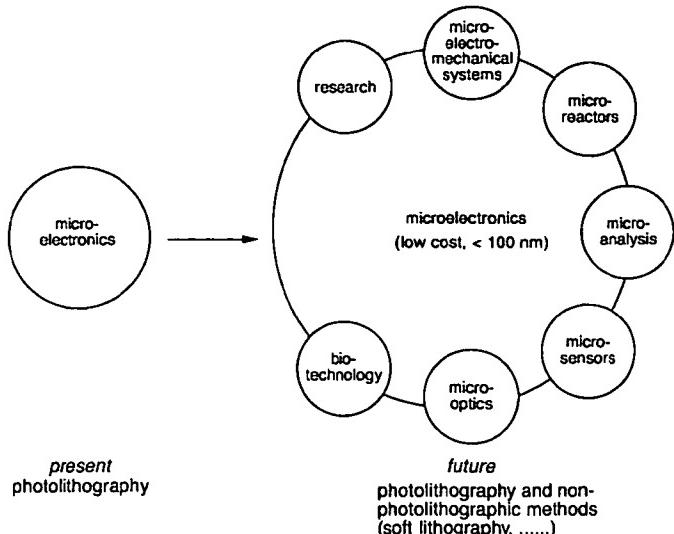


Figure 1. Microelectronics is based on photolithography and is very important, but the more expensive technology to surmount the "100-nm barrier"—a critical point in reducing feature sizes set by a combination of diffraction limitations to projected images and the lack of lenses that are transparent at wavelengths below 160 nm—make the future of photolithography on this small scale unclear. In addition, new opportunities in microfabrication are emerging as new types of Microsystems (right) are developed; for these opportunities, photolithography is not always the best option. For most applications, cost is a dominant parameter.

tained is approximately the wavelength (λ) of the light used. As a result, illuminating sources with shorter wavelengths are progressively introduced into photolithography to generate structures with smaller feature sizes (Table 1).^[10c] As structures become increasingly small, they also become increasingly difficult and expensive to produce.

In the late 1960s and early 1970s, Gordon Moore, founder of both Fairchild Semiconductor and Intel, projected that the number of transistors in an integrated circuit would double

Table 1. The recent past, present, and future of semiconductor technology.^[10c, 11]

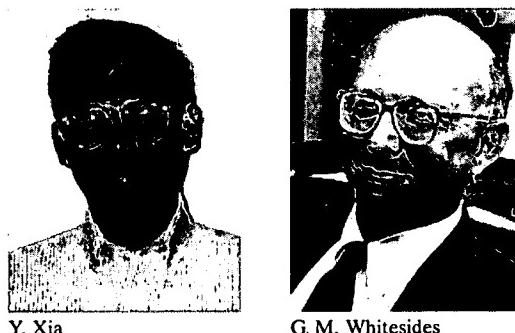
Year	Lithographic method	Resolution [nm] ^[a]	Bits (DRAM) ^[b]
<i>Photolithography (λ[nm])</i>			
1992	UV (436), <i>g</i> line of Hg lamp	500	16 M
1995	UV (365), <i>i</i> line of Hg lamp	350	64 M
1998	DUV (248), KrF excimer laser	250	256 M
2001	DUV (193), ArF excimer laser	180	1 G
2004	DUV (157), F ₂ excimer laser	120	4 G
2007	DUV (126), dimer discharge from an argon laser	100	16 G
2010	<i>Advanced lithography</i> extreme UV (EUV, 13 nm) soft X-ray (6–40 nm) focused ion beam (FIB) electron-beam writing proximal-probe methods	< 100 ^[c]	> 16 G

[a] The size of the smallest feature that can be manufactured. [b] The size of the dynamic random access memory (DRAM). [c] These techniques are still in early stages of development, and the smallest features that they can produce economically have not yet been defined.

every 18 months or so. This prediction was later known as Moore's Law.^[2] Over the past three decades many trends in the semiconductor industry have followed this law (Figure 2) thanks to continuous developments in photolithography that have allowed the size of features to decrease by a factor of approximately one-half every three years (Table 1). It is plausible that features as small as 100 nm can be manufactured optically in the future by employing advanced mask/resist technologies and deep UV (DUV) radiation.^[10d] Below this size, however, it is generally accepted that current strategies for photolithography may be blocked by optical diffraction and by the opacity of the materials used for making lenses or supports of photomasks. New approaches must be developed if Moore's Law is to extend into the range below

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George M. Whitesides was born in 1939 in Louisville, Kentucky, USA. He received an A.B. degree from Harvard University in 1960 and a Ph.D. degree from the California Institute of Technology (with J. D. Roberts) in 1964. He was a member of the faculty of the Massachusetts Institute of Technology from 1963 to 1982. He joined the Department of Chemistry of Harvard University in 1982 and was department chairman from 1986 to 1989; he is now Mallinckrodt Professor of Chemistry. His present research interests include biochemistry, surface chemistry, materials science, molecular virology, optics, self-assembly, bioanalytical chemistry, microelectromechanical systems, and microfluidics.



Y. Xia

G. M. Whitesides

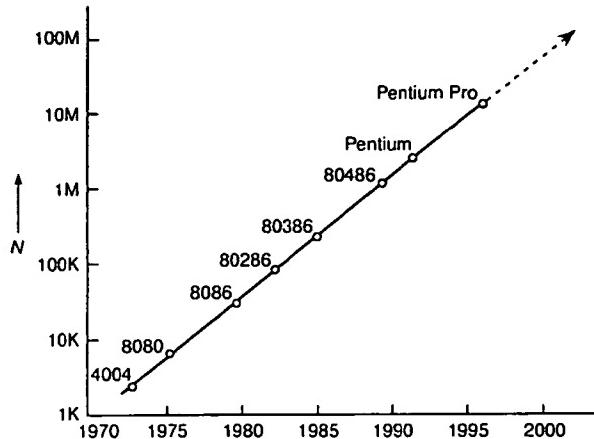


Figure 2. The integration trend given by Moore's law, and how microprocessors manufactured by Intel have followed this law since 1973.^[2b, c] N = number of transistors per chip. This curve reflects the general trend of miniaturization achieved by microlithography; it also applies to other devices such as RAMs, DRAMs, and Motorola microprocessors.

100 nm. Advanced lithographic techniques currently being explored for this regime include extreme UV (EUV) lithography, soft X-ray lithography, electron-beam writing, focused ion beam writing, and proximal-probe lithography.^[11, 12] These techniques are capable of generating very small features, but their development into practical commercial methods for low-cost, high-volume processing still requires great ingenuity: EUV and X-ray techniques, for example, will probably require the development of reflective optics.^[10d]

The continued shrinking of feature sizes toward 100 nm poses new technical challenges for photolithography, but, even for microfabrication on the micrometer scale, it may not be the only and/or best microfabrication method for all tasks. For example, it is expensive (both in capital and operating cost), which makes it less than accessible to chemists, biologists, and material scientists; it cannot be easily adopted for patterning nonplanar surfaces;^[13] it is largely ineffective in generating three-dimensional structures;^[11a] it is poorly suited for introducing specific chemical functionalities; it is directly applicable to only a limited set of materials used as photoresists;^[14] and it integrates well with semiconductor materials, but not necessarily with glass, plastics, ceramics, or carbon. These limitations suggest the need for alternative microfabrication techniques. The development of practical methods capable of generating structures smaller than 100 nm for a range of materials represents a major task, and is one of the greatest technical challenges now facing microfabrication.^[11, 12]

A number of non-photolithographic techniques have been demonstrated for fabricating (and in some cases for manufacturing) high-quality microstructures and nanostructures (Table 2).^[15–38] This review will focus on the soft lithographic techniques that we are currently exploring: microcontact printing (μ CP),^[34] replica molding (REM),^[35] microtransfer molding (μ TM),^[36] micromolding in capillaries (MIMIC),^[37] and solvent-assisted micromolding (SAMIM).^[38] Collectively, we call these techniques "soft lithography",^[33] because in each case an elastomeric stamp or mold is the key element that transfers the pattern to the substrate and, more broadly, because each uses flexible organic molecules and materials

Table 2. Non-photolithographic methods for micro- and nanofabrication.

Method	Resolution ^[a]	Ref.
injection molding	10 nm	[15, 16]
embossing (imprinting)	25 nm	[17, 18]
cast molding	50 nm	[19, 20]
laser ablation	70 nm	[21, 22]
micromachining with a sharp stylus	100 nm	[23]
laser-induced deposition	1 μ m	[24]
electrochemical micromachining	1 μ m	[25]
silver halide photography	5 μ m	[26]
pad printing	20 μ m	[27]
screen printing	20 μ m	[28]
ink-jet printing	50 μ m	[29, 30]
electrophotography (xerography)	50 μ m	[31]
stereolithography	100 μ m	[32]
<i>soft lithography</i>		[33]
microcontact printing (μ CP)	35 nm	[34, 84f]
replica molding (REM)	30 nm	[35]
microtransfer molding (μ TM)	1 μ m	[36]
micromolding in capillaries (MIMIC)	1 μ m	[37]
solvent-assisted micromolding (SAMIM)	60 nm	[38]

[a] The lateral dimension of the smallest feature that has been generated. These numbers do not represent ultimate limits.

rather than the rigid inorganic materials now commonly used in the fabrication of microelectronic systems (Table 3).

Soft lithography generates micropatterns of self-assembled monolayers (SAMs)^[39] by contact printing, and also forms microstructures in materials by embossing (imprinting)^[17, 18] and replica molding.^[19, 20] Figure 3 shows the general procedure for soft lithography in a technique we call "rapid prototyping" and whose components we describe in Section 2.5. The strength of soft lithography is in replicating rather than fabricating the master, but rapid prototyping and

Table 3. Comparison of photolithography to soft lithography.

	Photolithography	Soft lithography
definition of patterns	rigid photomask (patterned Cr supported on a quartz plate)	elastomeric stamp or mold (a PDMS block patterned with relief features)
materials that can be patterned directly	photoresists (polymers with photosensitive additives)	photoresists ^[e]
SAMs ^[a]		
unsensitized polymers ^[b–c] (epoxy, PU, PMMA, ABS, CA, PS, PE, PVC) ^[10]		
polymer precursors ^[c, d] (of carbon materials and ceramics)		
polymer beads ^[d]		
conducting polymers ^[d]		
colloidal materials ^[a, d]		
sol–gel materials ^[c, d]		
organic and inorganic salts ^[d]		
biological macromolecules ^[d]		
current limits	ca. 250 nm	see Table 2
to resolution		
minimum feature size	ca. 100 nm (?)	10 (?) – 100 nm

[a] μ CP. [b] REM. [c] μ TM. [d] MIMIC. [e] SAMIM. [f] PU: polyurethane; PMMA: poly(methyl methacrylate); ABS: poly(acrylonitrile-butadiene-styrene); CA: cellulose acetate; PS: polystyrene; PE: polyethylene; PVC: poly(vinyl chloride).

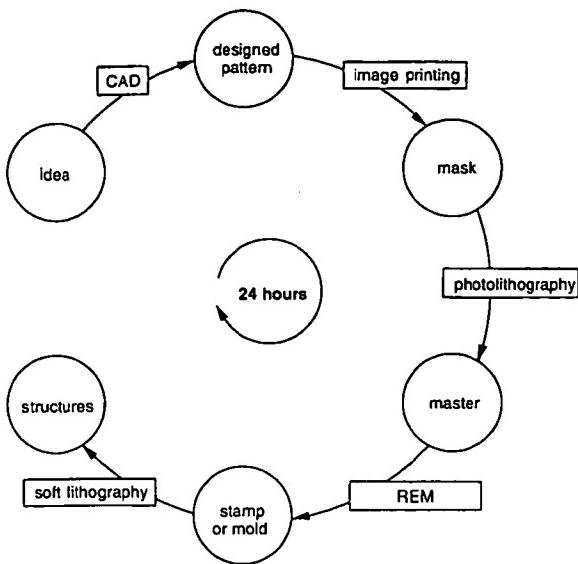


Figure 3. The rapid prototyping procedure for soft lithography. The pattern is composed and transferred to a CAD file, and printed on a transparent sheet of polymer with a commercial image setter. This patterned sheet is used in contact photolithography to prepare a master in a thin film of photoresist; a negative replica of this master in an elastomer becomes the stamp or mold for soft lithography. The overall procedure from design to stamp takes less than 24 hours to complete.

the ability to deform the elastomeric stamp or mold give it unique capabilities even in fabricating master patterns. Soft lithographic techniques require remarkably little capital investment and are procedurally simple: They can often be carried out in the ambient laboratory environment. They are not subject to the limitations set by optical diffraction and optical transparency (the edge definition is set, in principle, by van der Waals interactions and, in practice, by the properties of the materials involved), and they provide alternative routes to structures that are smaller than 100 nm without the need for advanced lithographic techniques. They also offer access to new types of surfaces, optical structures, sensors, prototype devices, and systems that could be difficult to fabricate by photolithographic procedures. Our aim in this review is to explain and examine the principles, processes, materials, and limitations of this new class of patterning techniques, and to describe their ability to form patterns and structures of a wide variety of materials with features that range from nanometers to micrometers in size.

2. Key Strategies of Soft Lithography

2.1. Self-Assembly

The obvious technical challenges to extending current photolithography to features that are smaller than 100 nm make it possible to at least consider radically new approaches to microfabrication. Both chemistry and biology can help in the development of new methodologies for microfabrication through contributions of a surprisingly broad range, both practical and conceptual. Among the conceptually new strategies offer possible routes to both smaller features and

lower costs, self-assembly has been the most fully explored and is closest to practical realization.^[40]

Self-assembly is the spontaneous organization of molecules or objects into stable, well-defined structures by noncovalent forces.^[40] The key idea in self-assembly is that the final structure is close to or at thermodynamic equilibrium; it therefore tends to form spontaneously and to reject defects. Self-assembly often provides routes to structures having greater order than can be reached in non-self-assembling structures. The final structure is predetermined by the characteristics of the initial subunits: The information that determines the final structure is coded in the structures and properties of the subunits (e.g., shapes and surface functionalities). Self-assembly is ubiquitous in nature:^[41] Processes such as folding of proteins and tRNAs as well as formation of the DNA double helix serve as biological illustrations of the potential of self-assembly in microfabrication. Various strategies of self-assembly have been developed and employed to fabricate two- and three-dimensional structures with dimensions ranging from molecular, through mesoscopic, to macroscopic sizes.^[42–45]

2.2. Self-Assembled Monolayers

Self-assembled monolayers (SAMs) are the most widely studied and best developed examples of nonbiological, self-assembling systems.^[39, 46] They form spontaneously by chemisorption and self-organization of functionalized, long-chain organic molecules onto the surfaces of appropriate substrates. SAMs are usually prepared by immersing a substrate in the solution containing a ligand that is reactive toward the surface, or by exposing the substrate to the vapor of the reactive species. Table 4 lists a number of systems known to give SAMs;^[47–65] new systems are still being developed.

The best characterized systems of SAMs are alkanethiolates $\text{CH}_3(\text{CH}_2)_n\text{S}^-$ on gold (Figure 4).^[47] Alkanethiols chemisorb spontaneously on a gold surface from solution and form adsorbed alkanethiolates. This process is assumed to occur with loss of dihydrogen; the fate of the hydrogen atom is still

Table 4. Substrates and ligands that form SAMs.

Substrate	Ligand or Precursor	Binding	Ref.
Au	RSH, ArSH (thiols)	RS-Au	[39, 46, 47]
Au	RSSR' (disulfides)	RS-Au	[39, 46, 48]
Au	RSR' (sulfides)	RS-Au	[39, 46, 49]
Au	RSO ₂ H	RSO ₂ -Au	[50]
Au	R ₃ P	R ₃ P-Au	[51]
Ag	RSH, ArSH	RS-Ag	[39, 52]
Cu	RSH, ArSH	RS-Cu	[39, 53]
Pd	RSH, ArSH	RS-Pd	[39, 54]
Pt	RNC	RNC-Pt	[39, 55]
GaAs	RSH	RS-GaAs	[56]
InP	RSH	RS-InP	[57]
SiO ₂ , glass	RSiCl ₃ , RSi(OR') ₃	siloxane	[39, 46, 58]
Si/Si-H	(RCOO) ₂ (neat)	R-Si	[59]
Si/Si-H	RCH=CH ₂	RCH ₂ CH ₂ Si	[60]
Si/Si-Cl	RLi, RMgX	R-Si	[61]
metal oxides	RCOOH	RCOO ⁻ ...MO _n ⁺	[62]
metal oxides	RCONHOH	RCONHOH...MO _n ⁺	[63]
ZrO ₂	RPO ₃ H ₂	RPO ₃ ²⁻ ...Zr ^{IV}	[64]
In ₂ O ₃ /SnO ₂ (ITO)	RPO ₃ H ₂	RPO ₃ ²⁻ ...M ⁺	[65]

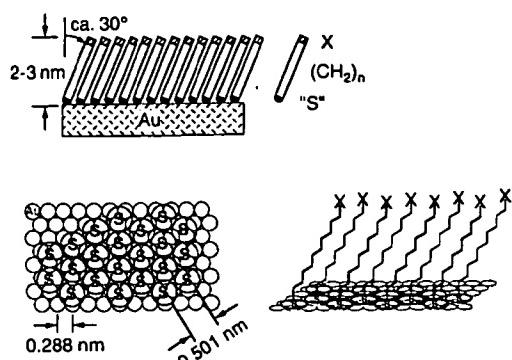
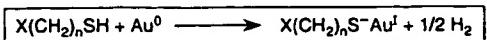


Figure 4. Representation of a highly ordered monolayer of alkanethiolate formed on a gold surface. The sulfur atoms form a commensurate overlayer on Au(111) with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, whose thickness is determined by the number of methylene groups (n) in the alkyl chain. The surface properties of the monolayer can be easily modified by changing the head group X . The alkyl chains $(CH_2)_n$ extend from the surface in a nearly all-*trans* configuration. On average they are tilted approximately 30° from the normal to the surface to maximize the van der Waals interactions between adjacent methylene groups.

not established. Sulfur atoms bonded to the gold surface bring the alkyl chains into close contact; these contacts freeze out configurational entropy and lead to an ordered structure. For carbon chains of up to approximately 20 atoms, the degree of interaction in a SAM increases with the density of molecules on the surface and the length of the alkyl backbones. Only alkanethiolates with $n > 11$ form the closely packed and essentially two-dimensional organic quasi-crystals supported on gold that characterize the SAMs most useful in soft lithography.^[46d] The formation of ordered SAMs on gold from alkanethiols is a relatively fast process: Highly ordered SAMs of hexadecanethiolate on gold can be prepared by immersing a gold substrate in a solution of hexadecanethiol in ethanol (ca. 2 mM) for several minutes, and formation of SAMs during microcontact printing may occur in seconds. This ability to form ordered structures rapidly is one of the factors that ultimately determine the success of microcontact printing.

The structures and properties of SAMs from alkanethiolates on gold have been examined using a number of techniques (Table 5).^[66–82] It is generally accepted that sulfur atoms form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer on the Au(111) surface (see Figure 4). Optical and diffraction techniques can only reveal the level of average order in SAMs (i.e., the dominant lattices and their dimensions) over the probed area (typically a few square millimeters). Recent STM studies show that these systems are heterogeneous and structurally complex: The alkyl chains may form a “superlattice” at the surface of the monolayer, that is, a lattice with a symmetry and dimension different from that of the underlying hexagonal lattice formed by sulfur atoms.^[46d] These results indicate that the order in the top part of SAMs is not dictated solely by the sulfur atoms directly bonded to the gold surface, but also depends strongly on the intermolecular interactions between the alkyl backbones. When alkanethiolates are terminated in head groups other than methyl, it becomes even more

Table 5. Techniques for characterizing SAMs of alkanethiolates on gold.

Property of SAMs	Technique	Ref.
structure and order	scanning probe microscopy	[66, 67]
	STM, AFM, LFM	[135]
	infrared spectroscopy	[39e, 68]
	low-energy helium diffraction	[69]
	X-ray diffraction	[70]
	transmission electron diffraction	[71]
	surface Raman scattering	[72]
	sum frequency spectroscopy (SFS)	[73]
	X-ray photoelectron spectroscopy (XPS)	[74]
	temperature programmed desorption (TPD)	[75]
composition	mass spectrometry (MS)	[76]
	contact angle	[77]
wettability	ellipsometry	[78]
	quartz crystal microbalance (QCM)	[79]
degree of perfection	surface acoustic wave (SAW) device	[80]
	electrochemical methods	[81]
defects	STM and AFM	[66, 67]
	wet etching	[82]

complicated to predict and determine the structures of the SAMs.

SAMs of alkanethiolates on gold exhibit many of the features that are most attractive about self-assembling systems: ease of preparation, density of defects low enough to be useful in many applications, good stability under ambient laboratory conditions, practicality in technological applications, and amenability to controlling interfacial properties (physical, chemical, electrochemical, and biochemical) of the system. As a result, SAMs are excellent model systems for studies on wetting, adhesion, lubrication, corrosion, nucleation, protein adsorption, and cell attachment.^[46, 83] SAMs are also well suited as ultrathin resists or passivating layers for fabrication of patterns and structures with lateral dimensions in the nanometer to micrometer range.

Patterning SAMs in the plane of the surface has been achieved by a wide variety of techniques (Table 6).^[84–104] Each technique has advantages and disadvantages. Only micro-

Table 6. Techniques that have been used for patterning SAMs.

Technique	SAMs	Resolution ^a	Ref.
microcontact printing (μCP)	RSH/Au	35 nm	[84]
	RSH/Ag	100 nm	[34, 84f, 85]
	RSH/Cu	500 nm	[87]
	RSH/Pd	500 nm	[88]
	RPO ₃ H ₂ /Al	500 nm	[89]
	siloxane/SiO ₂	500 nm	[90, 145]
photooxidation	RSH/Au	10 μm	[91]
photo-cross-linking	RSH/Au	10 μm	[92]
photoactivation	RSH/Au	10 μm	[93]
photolithography/plating	siloxane/glass	10 μm	[94]
	siloxane/SiO ₂	500 nm	[95]
electron-beam writing	RSH/Au	75 nm	[96]
	RSH/GaAs	25 nm	[97]
focused ion beam writing	siloxane/SiO ₂	5 nm	[98]
	RSH/Ag	10 μm	[99]
neutral metastable atom writing	RSH/Au	70 nm	[100]
	siloxane/SiO ₂	70 nm	[101]
SPM lithography	RSH/Au	10 nm	[84f, 102]
micromachining	RSH/Au	100 nm	[23, 103]
micropen writing	RSH/Au	10 μm	[104]

[a] The lateral dimension of the smallest feature that has been generated.

contact printing will be discussed in this review since it is the one that seems to offer the most interesting combination of convenience and new capability.

2.3. Contact Printing, Replica Molding, and Embossing

Contact printing is an efficient method for pattern transfer.^[105] A conformal contact between the stamp and the surface of the substrate is the key to its success. Printing has the advantage of simplicity and convenience: Once the stamp is available, multiple copies of the pattern can be produced using straightforward experimental techniques. Printing is an additive process; the waste of material is minimized. Printing also has the potential to be used for patterning large areas. Although contact printing is most suitable for two-dimensional fabrication, it has also been used to generate quasi-three-dimensional structures through combination with other processes such as metal plating.^[106]

Replica molding duplicates the information—for example, the shape, the morphology, and the structure—present in a master. It is a procedure that accommodates a wider range of materials than does photolithography. It also allows duplication of three-dimensional topologies in a single step, whereas photolithography is not able to replicate such structures. It has been used for the mass production of surface relief structures such as diffraction gratings,^[107] holograms,^[108] compact disks (CDs),^[19, 20] and microtools.^[109] Replica molding with an appropriate material (usually in the form of a precursor) enables highly complex structures in the master to be faithfully duplicated into multiple copies with nanometer resolution in a reliable, simple, and inexpensive way.^[110–112] The fidelity of replica molding is determined by van der Waals interactions, wetting, and kinetic factors such as filling of the mold. These physical interactions should allow more accurate replication of features that are smaller than 100 nm than does photolithography, which is limited by optical diffraction.^[10]

Embossing is another cost-effective, high-throughput manufacturing technique that imprints microstructures in thermoplastic materials.^[17, 18] The manufacturing of CDs based on imprinting in polycarbonate with nickel masters^[17a] and of holograms by imprinting in SURPHEX photopolymer (DuPont) with fused quartz masters^[17b] are two typical examples of large-volume commercial applications of this technique. Until recently embossing had not been seriously developed as a method for fabricating and manufacturing structures of semiconductors, metals, and other materials used in micro-electronic circuitry. The beautiful work by Chou et al. showed that embossing can be used to make features as small as 25 nm in silicon, and has attracted attention to the potential of this kind of patterning technique.^[18]

We are extending the capability of these patterning techniques by bringing new approaches and new materials into these areas. In particular, a combination of self-assembly (especially of self-assembled monolayers) and pattern transfer using elastomeric stamps, molds, or masks constitutes the basis of soft lithographic methods.^[33] It complements photolithography in a number of aspects and provides a wide range of new opportunities for micro- and nanofabrication.

2.4. Elastomeric Stamps and Masks

An elastomeric stamp, mold, or mask having relief structures on its surface is the key element of soft lithography.^[33–38] It is usually prepared by replica molding (Figure 5) by casting

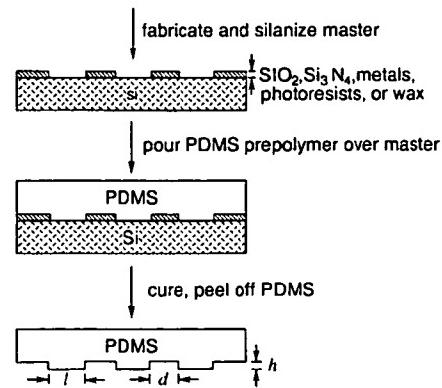


Figure 5. Schematic illustration of the procedure for casting PDMS replicas from a master having relief structures on its surface. The master is silanized by exposure to $\text{CF}_3(\text{CF}_2)_8(\text{CH}_2)_3\text{SiCl}_3$ vapor (ca. 0.5 h); each master can be used to fabricate more than 50 PDMS replicas. Representative ranges of values for h , d , and l are 0.2–20, 0.5–200, and 0.5–200 μm , respectively.

the liquid prepolymer of an elastomer against a master that has a patterned relief structure in its surface. The elastomer we used in most demonstrations is poly(dimethylsiloxane) (PDMS),^[113] for example, Sylgard 184 from Dow Corning. We and other groups have also used other elastomers such as polyurethanes, polyimides, and cross-linked Novolac resin (a phenol formaldehyde polymer).^[84, 85]

Several properties of PDMS are instrumental in the formation of high-quality patterns and structures in soft lithography. First, PDMS is an elastomer and conforms to the surface of the substrate over a relatively large area. PDMS is deformable enough such that conformal contact can even be achieved on surfaces that are nonplanar on the micrometer scale.^[114] The elastic characteristic of PDMS also allows it to be released easily, even from complex and fragile structures. Second, PDMS provides a surface that is low in interfacial free energy (ca. $21.6 \times 10^{-3} \text{ J m}^{-2}$) and chemically inert.^[113] Polymers being molded do not adhere irreversibly to or react with the surface of PDMS. Third, PDMS is homogeneous, isotropic, and optically transparent down to about 300 nm.^[115] UV cross-linking of prepolymers that are being molded is possible. It has been used to construct elastomeric optical devices for adaptive optics^[116–119] and to fabricate photomasks for use in UV photolithography^[120] and contact phase-shift photolithography.^[121] Fourth, PDMS is a durable elastomer. We used the same stamp up to about 100 times over a period of several months without noticeable degradation in performance.^[85] Fifth, the surface properties of PDMS can be readily modified by treatment with plasma followed by the formation of SAMs (Figure 6) to give appropriate interfacial interactions with materials that themselves have a wide range of interfacial free energies.^[122]

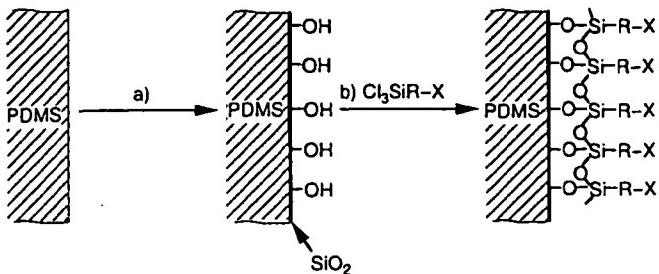


Figure 6. Schematic procedure for the modification of the PDMS surface. a) Treatment with an O_2 plasma; b) reaction with silyl chloride vapor. Different terminal groups X of the SAMs give different interfacial properties.^[122]

The elastomeric character of PDMS is also the origin of some of the most serious technical problems that must be solved before soft lithography can be used in forming complex patterned structures (Figure 7). First, gravity, adhesion and

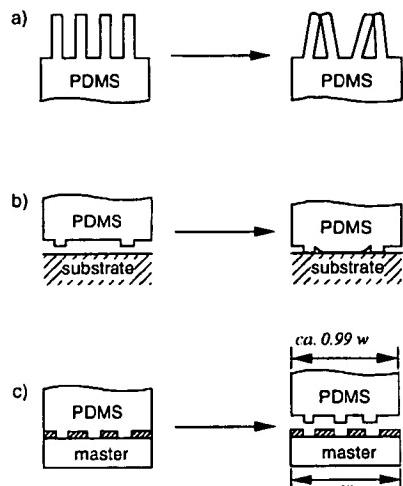


Figure 7. Schematic illustration of possible deformations and distortions of microstructures in the surfaces of elastomers such as PDMS. a) Pairing, b) sagging, c) shrinking.

capillary forces^[123] exert stress on the elastomeric features and cause them to collapse and generate defects in the pattern that is formed.^[124] If the aspect ratio of the relief features is too large, the PDMS microstructures fall under their own weight or collapse owing to the forces typical of inking or printing of the stamp. Delamarche et al. showed that the aspect ratios (l/h , Figure 5) of the relief structures on PDMS surfaces had to be between about 0.2 and 2 in order to obtain defect-free stamps.^[124] They also found that collapsed parallel lines in PDMS could be restored by washing the stamp with sodium dodecylsulfate (SDS, ca. 1% in water) followed by rinsing with heptane. Second, when the aspect ratios are too low, the relief structures are not able to withstand the compressive forces typical of printing and the adhesion between the stamp and the substrate; these interactions result in sagging. This deformation excludes soft lithography for use with patterns in which features are widely separated ($d \geq 20h$, Figure 5), unless nonfunctional "posts" can be introduced into the designs to support the noncontact regions. Third, achieving

accurate registration without distorting the multilayer fabrication process is substantially more difficult with a flexible elastomer than with a rigid material. There are several other disadvantages that may limit the performance of PDMS for certain types of applications. For example, PDMS shrinks by a factor of about 1% upon curing,^[125] and PDMS can be readily swelled by nonpolar solvents such as toluene and hexane.^[113, 126] We and other groups are beginning to address these problems associated with elastomeric materials: We recently found that we could use the Moiré technique to determine distortions of PDMS stamps or molds during soft lithography, and a method was identified for limiting the maximum distortions to less than 1 μm over areas of about 1 cm^2 .^[127] We believe that we will find solutions for most of these problems in the future by using new materials, new designs, and new configurations.

2.5. Masters and Rapid Prototyping

The utility of soft lithographic techniques is often limited by the availability of appropriate masters. In general, the master used to cast the PDMS stamp or mold is fabricated using microlithographic techniques such as photolithography^[84] or micromachining,^[128] or from available relief structures such as diffraction gratings or TEM grids.^[129] Photolithography seems to be the most convenient method for generating complex patterns. Chrome masks are commercially available, but they are expensive (ca. \$200 per square inch for features larger than 5 μm and ca. \$500 per square inch for features between 1 and 5 μm). The time and expense involved in generating chrome masks are significant barriers to the use of photolithography by chemists and biologists. These barriers have also limited the development of soft lithography, and inhibited the use of microfabrication in a number of areas.

Recently we^[130] and other groups^[131] developed a system that allows fabrication of masters having feature sizes that are greater than or equal to 20 μm rapidly and at low cost (see Figure 3). In this technique we draw patterns using computer programs such as Freehand or AutoCAD and print them directly onto polymer sheets with a commercial laser-assisted image-setting system (e.g., Herkules PRO, resolution of 3387 dpi (dots per inch), Linotype-Hell Company, Hauppauge, NY). With this method photomasks, transparent polymeric sheets patterned with microstructures of black ink, can be made in a few hours at a cost of about \$1 per square inch. Although these masks do not have the durability and dimensional stability required for use in the manufacturing of microelectronic devices, they are suitable for the rapid production of simple patterns that are well suited for prototyping microfluidic, microoptical, and microanalytical systems as well as for sensors.^[5-9, 130] After the patterns on these polymer films are transferred into films of photoresists coated on silicon substrates using photolithography and developing, the resulting patterns can serve as masters to make the required PDMS stamps. Rapid prototyping allows the production of substantial numbers of simple microstructures rapidly and inexpensively. By combining this method with soft lithographic techniques, we can fabricate patterned

microstructures of polymers and metals within 24 hours after the design is completed. At present, the smallest feature size that can be achieved directly using this procedure is about 20 μm , a value that is limited by the resolution (ca. 3387 dpi) of the image-setting system. It should be possible to generate smaller features by using printers with higher resolutions. We believe that rapid prototyping paves the way for expanded use of microfabrication in chemistry and biology, especially when patterns may be complex but require only modest feature sizes.

3. Microcontact Printing

3.1. Principles of Microcontact Printing

Microcontact printing (μCP) is a flexible, non-photolithographic method that routinely forms patterned SAMs containing regions terminated by different chemical functionalities with submicron lateral dimensions.^[84] The procedure is remarkably simple (Figure 8). An elastomeric PDMS stamp is

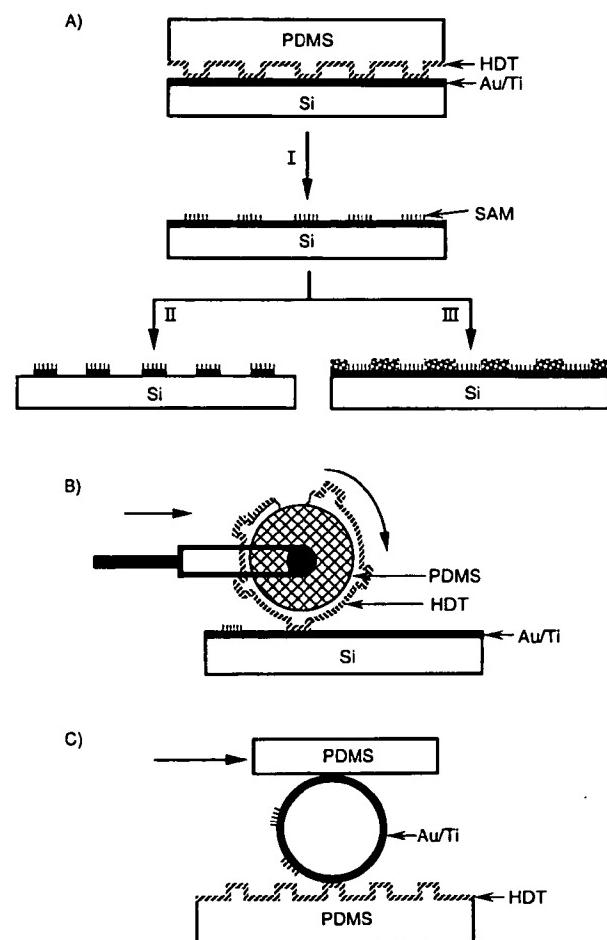


Figure 8. Schematic illustration of procedures for μCP of hexadecanethiol (HDT) on a gold surface: A) printing on a planar surface with a planar stamp (I: printing of the SAM, II: etching, III: deposition);^[84] B) large-area printing on a planar surface with a rolling stamp;^[147] C) printing on a nonplanar surface with a planar stamp.^[149] After the “ink” (ca. 2 mm HDT in ethanol) was applied to the PDMS stamp with a cotton swab, the stamp was dried in a stream of N_2 (ca. 1 min) and then brought into contact with the gold surface (ca. 10–20 s).

used to transfer molecules of the “ink” to the surface of the substrate by contact. After printing, a different SAM can be formed on the underderivatized regions by washing the patterned substrate with a dilute solution containing the second molecule. Microcontact printing was first demonstrated for SAMs of alkanethiolates on gold.^[34] Its success relies on the rapid reaction of alkanethiols on gold and on the “autophobicity” of the resulting SAMs.^[132] An exceptionally thoughtful STM study by Larsen et al. showed that for μCP with solutions of dodecanethiol in ethanol with concentrations greater than or equal to 10 mM, a contact time of longer than 0.3 s was enough to form highly ordered SAMs on Au(111) that are indistinguishable from those formed by adsorption from solution (Figure 9).^[80f, 133] For μCP with hexadecanethiol (ca. 2 mM in ethanol), a contact time of about 10–20 s is usually used.^[84]

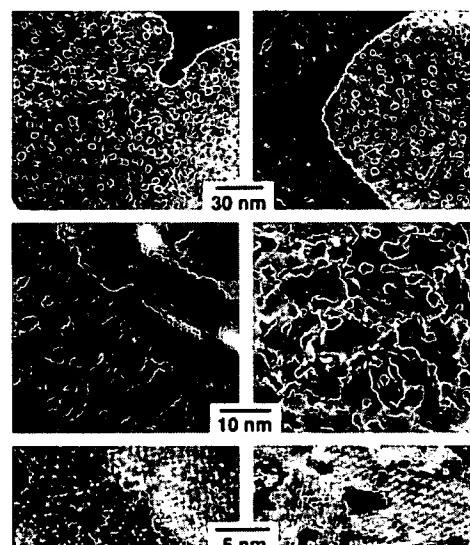


Figure 9. Comparison of STM images of SAMs of dodecanethiol (DDT) on Au(111) formed by μCP (left) and by adsorption from solution (right). The μCP was carried out with a solution of DDT in ethanol (ca. 100 mM) as the “ink” (the stamp was in contact with the gold surface for about 10 s); in the case of adsorption from solution the gold surface was equilibrated with a solution of DDT in ethanol (1 mM) for about 18 h (taken from Larsen et al.^[133]).

Patterned SAMs formed by μCP can be visualized using a range of techniques such as scanning electron microscopy (SEM),^[134] scanning probe microscopy (SPM),^[135] secondary ion mass spectrometry (SIMS),^[136] condensation figures (CFs),^[136] and surface-enhanced Raman microscopy.^[86b] Figure 10 compares the pattern in an original master with that of a SAM of hexadecanethiolate on gold formed by μCP with a PDMS stamp cast from this master. Figure 11 shows lateral force microscopy (LFM) images of a test pattern of SAMs of hexadecanethiolate on gold.^[135b] The patterned SAMs of hexadecanethiolate formed by μCP seem to have an edge roughness less than about 50 nm.

We and other groups have extended μCP to a number of other systems of SAMs (see Table 6). The most useful systems are patterned SAMs of alkanethiolates on evaporated thin films of gold and silver, because both systems give highly ordered monolayers. Gold is interesting since it is widely used

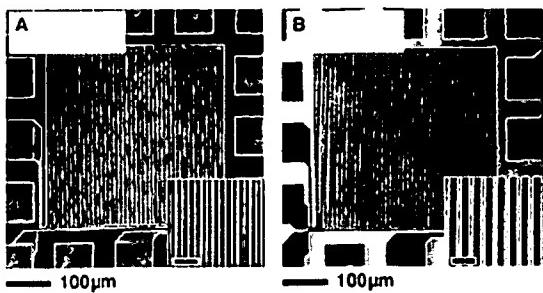


Figure 10. SEM images (at two different magnifications) of A) a master and B) the pattern of a SAM of HDT on gold formed by μ CP (contact time ca. 10 s) with a PDMS stamp cast from this master. A planar PDMS stamp was used. The contrast in the image of the master (A) resulted from different heights and/or materials between regions. The dark regions on the SAM-patterned surface in image B represent the SAM of HDT, and the light regions underivatized gold. The scale bars in the insets correspond to 10 μ m.

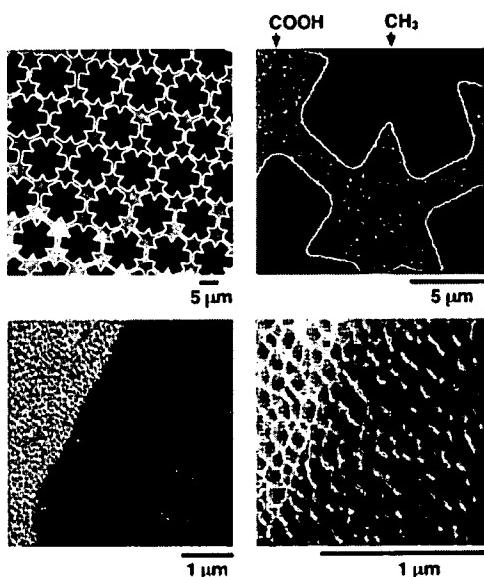


Figure 11. LFM images (at four different magnifications) of a gold surface patterned with SAMs terminated in different head groups. The surface was printed in HDT; the remaining regions were then derivatized with HS(CH₂)₅COOH by immersing the patterned sample in a solution containing the second thiol. Relatively high frictional forces between the probe and the surface were detected in regions covered with a COOH-terminated SAM (light), and relatively low frictional forces were measured over regions covered with a CH₃-terminated SAM (dark).^[135b]

as the material for electrodes in many applications,^[137] and it is compatible with microelectronic devices based on GaAs (but not on silicon).^[138] Silver is attractive because it is more convenient to etch than gold: Silver is chemically more reactive than gold and therefore dissolves more rapidly in most etchants;^[86] the level of defects in SAMs of alkanethiolates on silver also seems to be lower than on gold.^[86] Furthermore, silver is an excellent electrical and thermal conductor.^[139] The system of siloxanes on HO-terminated surfaces is less tractable and usually gives disordered SAMs and in some cases submonolayers or multilayers.^[140]

Patterned SAMs can be used as ultrathin resists in selective wet etching^[84, 141] or as templates to control the wetting, dewetting, nucleation, growth, and deposition of other materials (Figure 8 A, II and III).^[142–145] They have also been

used as supports to control both azimuthal and polar orientations of nematic liquid crystals (LCs).^[146] The smallest features generated to date with a combination of μ CP and selective etching are trenches etched in gold with lateral dimensions of approximately 35 nm.^[84f] The minimum size of features that can be fabricated by μ CP has still not been completely defined. Because the SAMs are only 1–3 nm thick, there is little loss in edge definition due to the thickness of the resist; the major determinants of edge resolution seem to be the fidelity of the contact printing and the anisotropy in the etching of the underlying metal. Absorbates on the surface of the substrate, the roughness of the surface, and materials properties (especially the deformation and distortion) of the elastomeric stamp also influence the resolution and feature size of patterns formed by μ CP. Some tailoring of the properties of the PDMS stamp or development of new elastomeric materials optimized for the regime below 100 nm will be useful.

Microcontact printing is attractive because it is simple, inexpensive, and flexible. Routine access to clean rooms is not required (at least for fabricating structures that are larger than 20 μ m by rapid prototyping and similar techniques), although occasional use of these facilities is convenient for making masters. The process is inherently parallel—that is, it forms the pattern over the entire area of the substrate in contact with the stamp at the same time—and thus suitable for forming patterns over large areas ($\geq 50 \text{ cm}^2$) in a single impression (Figure 8 B).^[147] The elastomeric PDMS stamp and the surface chemistry for the formation of SAMs can be manipulated in a number of ways to reduce the size of features generated by μ CP.^[148] It can, in principle, be used for many micro- and nanofabrication tasks and is a low-cost process. In particular, it can be applied to types of patterning where optically based lithography simply fails, for example, patterning nonplanar surfaces.^[149]

3.2. Patterned SAMs as Ultrathin Resists in Selective Wet Etching

SAMs do not have the durability to serve as etch masks in conventional reactive-ion etching.^[150] They are, however, efficient resists for certain types of wet etchants. Table 7 summarizes selective chemical etchants that have been studied for use with patterned SAMs.^[84, 141] Many other selective etches are known for these and other materials, and they remain to be explored in conjunction with SAMs.^[151]

Figure 12 shows SEM images of a series of test patterns of silver that were fabricated by μ CP with hexadecanethiol followed by selective etching in aqueous solutions of ferricyanide.^[86a] The SAM-derivatized regions were barely attacked by the etchant within the time required to remove the bare regions. These images represent the level of complexity, perfection, and scale that can be produced *routinely* with μ CP. The ability to generate arrays of microstructures of coinage metals with controlled shapes and dimensions is directly useful in fabricating arrays of microelectrodes for sensors^[8] and other electrochemical devices.^[137] Another application of μ CP is in the preparation of gold or silver patterns to be used

Table 7. Selective etchants that have been used with patterned SAMs generated by μ CP (all wet etchants were used in aqueous solutions).

Surface	SAM	Etchant (approximate pH)	Ref.
Ag	RS ⁻	K ₂ S ₂ O ₈ /K ₃ [Fe(CN) ₆]/K ₄ [Fe(CN) ₆] (14)	[84, 85, 141]
		KCN/O ₂ (14)	[34, 84, 85]
		CS(NH ₂) ₂ /H ₂ O ₂ (1)	[84e, 141]
		Fe(NO ₃) ₃ (6)	[84e, 86a]
		K ₂ S ₂ O ₈ /K ₃ [Fe(CN) ₆]/K ₄ [Fe(CN) ₆] (7)	[84e, 86a, 141]
		NH ₄ OH/K ₃ [Fe(CN) ₆]/K ₄ [Fe(CN) ₆] (12)	[84e, 86a]
Cu	RS ⁻	NH ₄ OH/H ₂ O ₂ (12)	[84e, 86a]
		NH ₄ OH/O ₂ (12)	[84e, 86a]
		KCN/O ₂ (14)	[84e, 86a, 141]
		FeCl ₃ /HCl (1)	[84e, 87b]
GaAs	RS ⁻	FeCl ₃ /NH ₄ Cl (6)	[84e, 87b]
		H ₂ O ₂ /HCl (1)	[84e, 87a]
		HCl/HNO ₃ (1)	[84e, 97]
Pd	RS ⁻	HCl/HNO ₃ (1)	[88]
Al	RPO ₃ ⁻	HCl/HNO ₃ (1)	[89]
Si/SiO ₂	RSiO ₃ ⁻ ^[4]	HF/NH ₄ F (2)	[90b]
glass	RSiO ₃ ⁻ ^[4]	HF/NH ₄ F (partially selective)	[90b]

[a] These SAMs are formed by contact of RSiCl₃ or RSi(OCH₃)₃ with the substrates.

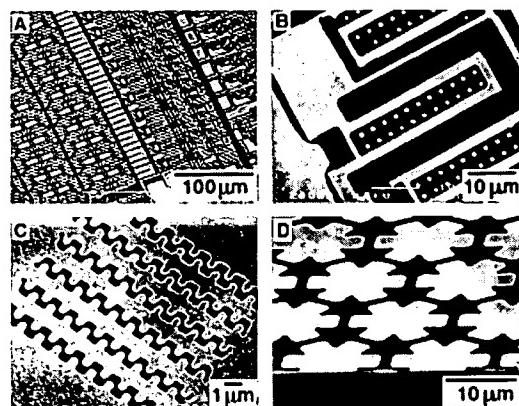


Figure 12. SEM images of test patterns on layers of silver (A, B, C: 50 nm thick; D: 200 nm thick) that were fabricated by μ CP with HDT followed by chemical etching in an aqueous solution of ferricyanide. The patterns in A and B were printed with rolling stamps,^[147] and those in C and D with planar stamps.^[86a] The bright regions represent silver, and the dark regions Si/SiO₂ in which unprotected silver has dissolved.

as secondary masks in the etching of underlying substrates such as SiO₂, silicon, and GaAs.^[152, 153] Figure 13 shows SEM images of microstructures in silicon that were fabricated by anisotropic etching of Si(100) in an aqueous solution containing KOH and 2-propanol with patterns of silver (50 nm thick) as masks.^[86a, 154] The silver masks were in turn generated with a combination of μ CP of hexadecanethiol and selective chemical etching.

SAMs and patterning by μ CP illustrate a new approach to microfabrication. Although this combination is proving immediately useful in single-layer fabrication (e.g., sensors and microelectrode arrays), several issues remain to be solved before it can be considered for application in complex microelectronics. For example, the formation and distribution of defects in SAMs, especially under the conditions of chemical etching, must be understood. A recent study based on a method involving two-stage chemical amplification found that the density of defects in SAMs depended on the

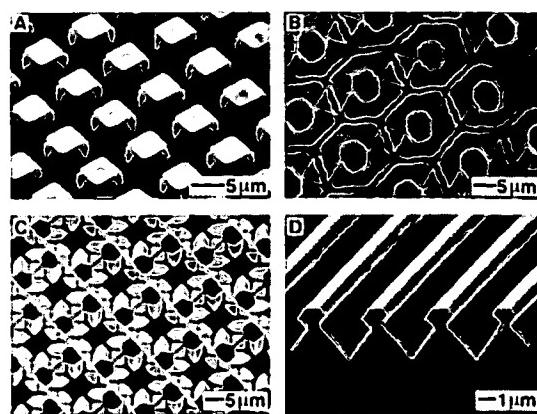


Figure 13. SEM images of silicon structures generated by anisotropic etching of Si(100) with patterned structures of silver or gold as masks.^[86a, 120] The metal mask is still on the surface in A; it has been removed by immersion in aqua regia for B, C, and D. The structure in D was fabricated by a combination of shadow evaporation and anisotropic etching of Si(100).^[153]

thickness of the gold layer, the length of the alkyl chain, and the conditions used for preparing the SAMs.^[82] The density of defects in printed SAMs (in terms of pinholes in SAM-derivatized regions) measured using this technique was about 10³ pits per mm² for 50 nm thick gold, and about 10 pits per mm² for 50 nm thick silver.^[155] These densities are still too high to be useful for fabricating high-resolution microelectronic devices. The latter is, however, low enough that silver lines (200 nm thick and 50 μ m wide) extending approximately 5 m in length are electrically continuous with no evidence of electrically significant defects.^[130] The patterned microstructures fabricated using this procedure are acceptable for applications in many areas other than microelectronics, including the production of microelectromechanical systems (MEMS),^[5] microanalytical systems,^[6] sensors,^[8] solar cells,^[156] and optical components.^[152b, 157]

3.3. Patterned SAMs as Passivating Layers in Selective Deposition

Through chemical control of the length of the polymethylene chain, the thickness of a SAM can be predetermined with a precision of about 0.1 nm. Organic synthesis also makes it possible to incorporate different functional groups (e.g., fluorocarbons, acids, esters, amines, amides, alcohols, nitriles, and ethers) into and/or at the termini of the alkyl chain.^[39] With μ CP, SAMs with different functional head groups can be organized into different patterns on a single surface and employed to control wetting, dewetting, nucleation, or deposition of other materials on this surface.^[142–145]

Figures 14 A and 14 B shows how functionalities of SAMs influence the wetting and dewetting of liquids on SAM-patterned surfaces. These processes are determined by the minimization of free energies. They use self-assembly at two scales: the formation of SAMs at the molecular scale and the fabrication of structures of liquids at the mesoscopic scale. Figure 14 A shows an optical micrograph of drops of water preferentially condensed on hydrophilic regions of a surface

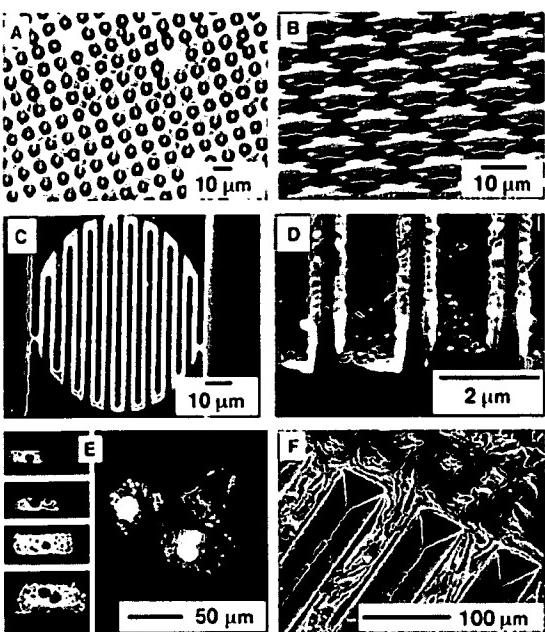


Figure 14. Demonstration of selective nucleation and deposition with patterned SAMs as templates. A) An optical micrograph of water condensed on a SAM-patterned gold surface.^[142a] B) An SEM image of microstructures of polyurethane assembled by selective dewetting;^[142b] only COOH-terminated regions were covered by water or polyurethane liquid. C) An SEM image of microstructures of LiNbO_3 on Si/SiO_2 produced with selective CVD.^[145b] D) An SEM image of copper microstructures formed in silicon microtrenches with selective CVD.^[145a] LiNbO_3 and copper only nucleated and grew on bare regions of SiO_2 underivatized by CH_3 -terminated siloxane SAMs. E) Optical micrographs of hepatocytes placed on SAM-patterned (left) and bare surfaces (right).^[143a] F) An SEM image of mammalian cells selectively attached to the plateaus of a contoured surface.^[143b] In E and F the surfaces were derivatized by μCP in such a way that certain regions of the surface terminated in methyl groups whereas others terminated in oligo(ethylene glycol) groups. The matrix protein (fibronectin) only adsorbed to the methyl-terminated regions, and cells only attached to those regions where the matrix proteins were adsorbed.

patterned with SAMs terminated in carboxylic (COOH) and methyl groups (CH_3); no water condensed on the hydrophobic regions.^[142a] Figure 14B shows an SEM image of patterned microstructures of polyurethane (PU) formed by selective dewetting.^[142b] The liquid prepolymer of PU placed on the SAM-patterned surface selectively dewetted those regions derivatized with methyl groups (CH_3) and formed patterned structures on the hydrophilic regions terminated in hydroxyl groups (CH_2OH). The prepolymer was then solidified by curing under UV light. The organization of liquids into patterned arrays illustrates the use of controlled wettability in microfabrication. These patterned microstructures of polymers have been used as arrays of microlenses^[142b] and optical waveguides.^[142f]

Nuzzo et al. demonstrated selective chemical vapor deposition (CVD)^[158] on Si/SiO_2 with printed SAMs of siloxanes as templates (Figures 14C, D).^[145] The patterned SAMs directed the selective CVD by inhibiting nucleation: The material to be patterned only nucleated and grew on the bare regions underivatized with SAMs and formed continuous structures. This procedure could in principle be used to deposit a variety of materials selectively on many substrates without photo-

lithography. The selective CVD of Cu may be useful in microelectronics processing, including the fabrication of thin-film interconnects (with feature sizes of ca. 0.5–100 μm) and selective filling of trenches and vias (representative microstructures having high aspect ratios) with feature sizes below about 1 μm .^[159]

Patterned SAMs have also been used as templates to define and control the adsorption of extracellular matrix proteins and consequently the attachment of mammalian cells.^[143] This technique makes it possible to place cells in predetermined locations in an array with defined shapes, sizes, and distances of separation. Figures 14E and 14F show SEM images of cells that have been selectively attached to a planar^[143a] and a contoured surface,^[143b] respectively. Using simple patterning procedures, it is possible to dictate the shape assumed by a cell that attaches to a surface and thus to control certain aspects of cell growth and protein secretion. This technique allows us to examine the influence of cell morphology on cell metabolism,^[143d] and should be useful for applications in biotechnology that require analysis of individual cells cultured at high density and/or repeated access to cells placed in specified locations. The results of these studies may eventually shed light on complex phenomena such as contact inhibition of cell proliferation, or they may lead to new analytical systems based on arrays of cells.

3.4. Formation of Microstructures on Nonplanar Surfaces

Patterning on nonplanar surfaces has been a substantial challenge for photolithography and related techniques: even gently curved surfaces often cannot be patterned by photolithography because of limitations to depth of focus.^[13] Because μCP involves conformal contact using an elastomeric stamp, it offers immediate advantages over photolithography in patterning nonplanar surfaces.^[149]

Figure 8C illustrates one method for forming patterned microfeatures on surfaces of capillaries. A piece of flat PDMS stamp is used to control the movement of the capillary. Figures 15A and 15B show SEM images of test patterns of gold that were formed on gold-coated glass capillaries by μCP with hexadecanethiol followed by selective etching in an aqueous solution of cyanide.^[149] They clearly show well-defined features of gold with dimensions of a few microns on capillaries with radii of curvature of about 500 μm (Figure 15A) and about 50 μm (Figure 15B). Microcontact printing can generate microstructures on planar and nonplanar surfaces with similar edge resolution. At present, there is no comparable technique for microfabrication on curved surfaces. Our recent demonstration of using electroless deposition rather than metal evaporation for preparing thin films of silver as the substrates for μCP of alkanethiols further simplifies the procedure for patterning nonplanar surfaces (even hidden surfaces such as the inside surfaces of hollow glass tubes).^[114] The procedure based on μCP opens the door immediately to new types of electronic, optical, MEMS, and analytical structures including microtransformers (Figure 15C),^[160] current carriers in microinductors,^[160] microsprings

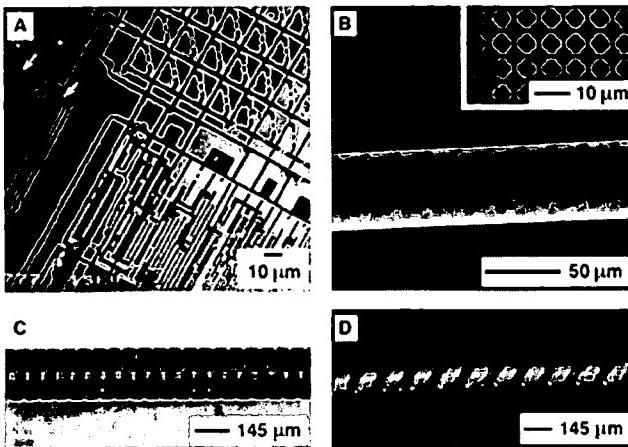


Figure 15. A, B) SEM images of test patterns of gold on curved surfaces (curvature 500 and 50 μm , respectively) that were fabricated by μCP with HDT followed by selective etching in an aqueous solution of KCN saturated with O_2 .^[149] C, D) Optical micrographs of a microtransformer^[160] and a microspring^[161] fabricated by μCP with HDT on silver (coated on the capillaries) followed by selective etching of silver and electroplating of nickel (C) and copper (D). The arrows in A indicate two defects caused by sagging.

(Figure 15D),^[161] in-fiber notch filters and Bragg gratings,^[162] micro-coils for high-resolution NMR spectroscopy,^[163] and intravascular stents.^[164]

3.5. Microcontact Printing of Other Materials

Microcontact printing seems to be a general method for forming patterns of a variety of materials on surfaces of solid substrates through contact pattern transfer. We demonstrated μCP of protonic acids^[165] and liquids containing suspended palladium colloids^[106, 166] using similar procedures. Protonic acids were printed onto thin films of acid-sensitive photoresist.^[167] They acted as the catalyst for the decomposition of the photoresist upon heating: Regions sensitized by acids became soluble in the basic developing solution. Colloids were also printed directly on a variety of substrates including glass, Si/SiO₂, and polymer films.^[106, 166] The deposited colloids acted as catalysts for electroless deposition of metals (Figure 16). Microcontact printing of aqueous solutions containing biological molecules (e.g., proteins and enzymes) might also be possible, although formation of uniform monolayers of such materials using printing might be difficult.



Figure 16. An SEM image of copper microstructures that were fabricated by electroless plating onto a pattern of electrocatalytic colloid particles of palladium. The palladium pattern was printed by μCP .^[106]

4. Micromolding and Related Techniques

4.1. Replica Molding

Our procedure for replica molding (REM; Figure 17A) differs from conventional procedures in the use of an elastomeric mold rather than a rigid mold.^[35, 168] The elasticity

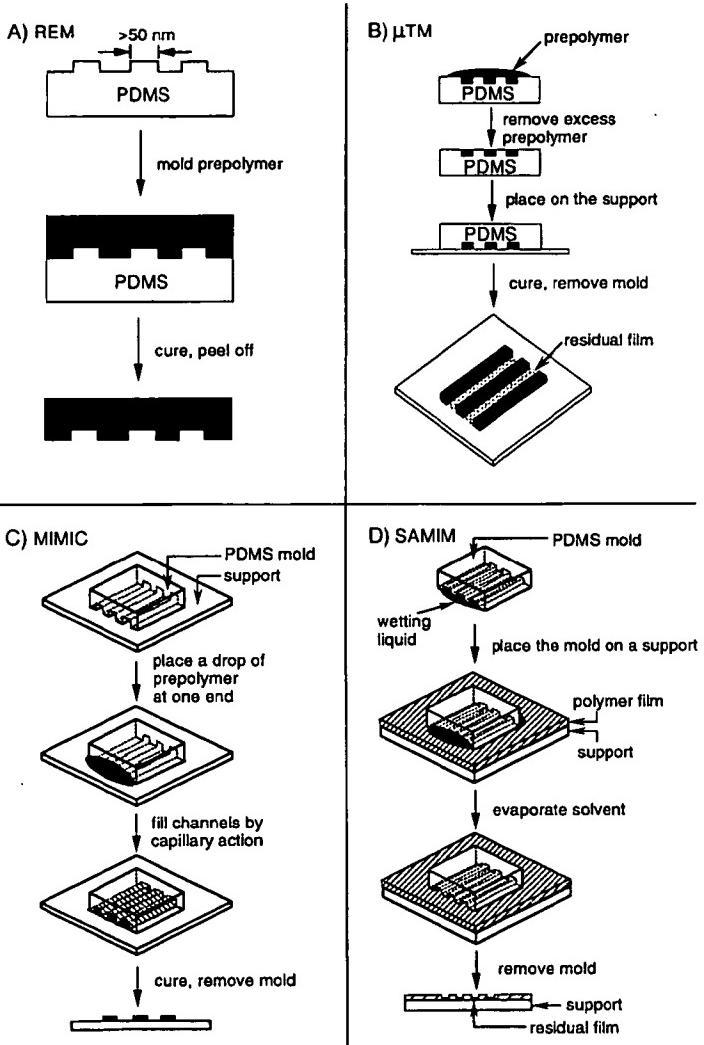


Figure 17. Schematic illustration of procedures for A) replica molding, B) microtransfer molding, C) micromolding in capillaries, and D) solvent-assisted micromolding.

and low surface energy of the elastomeric PDMS mold allows it to be released easily. An elastomeric mold also offers the opportunity to manipulate the size and shape of features present on the mold by mechanical deformation. The capability and versatility of this new procedure has been demonstrated for nanomanufacturing.^[169] Conventional high-resolution nanolithographic techniques would be used to make masters, and these structures would then be duplicated into multiple copies by replica molding with organic polymers. This technique has also been adapted for the fabrication of topologically complex, optically functional surfaces that would be difficult to fabricate with other techniques.^[35]

4.1.1. Nanomanufacturing

We demonstrated that replica molding against elastomeric molds is possible with a resolution on the nanometer scale.^[169] Figure 18 shows AFM images of chromium structures on a

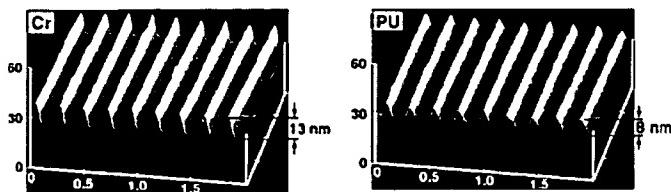


Figure 18. AFM images of chromium structures on a master and a PU replica prepared from a PDMS mold cast from this master.^[169] The width is given in micrometers; the depth and height are given in nanometers.

master^[170] and a PU replica prepared from a PDMS mold cast against this master. The most important feature of this replicated PU is the accuracy with which the vertical dimension is reproduced. The heights of the chromium lines on the original master were about 13 nm; the heights of the PU lines were about 8 nm. The prepolymer of PU used here shrinks less than 3% upon curing.^[171] These images demonstrate that, within our ability to compare similar structures, this replica molding procedure duplicated structures within a few nanometers over substantial areas (ca. 1 mm²).

We also monitored the quality of the replica structures generated from successive molds prepared from the same master.^[169] Figure 19A shows the AFM image of gold structures on a master before it was used to cast PDMS molds; the gold master was prepared using a procedure including electron-beam writing in a resist, development of the lines, metal evaporation, and lift-off. Figure 19B shows an

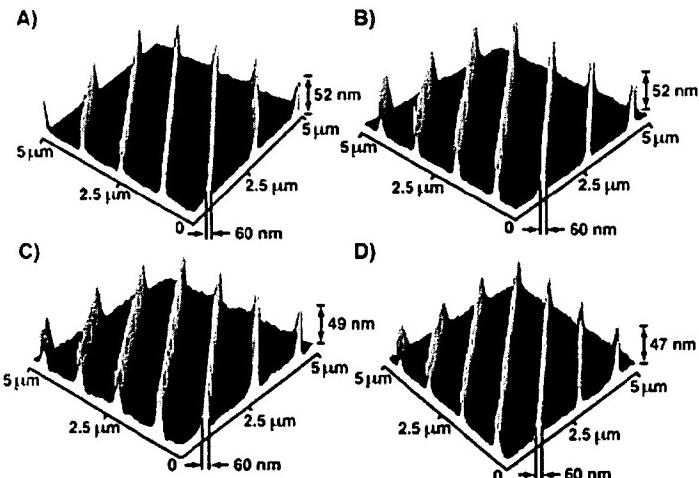


Figure 19. A, B) AFM images of gold structures on a master A) before it was used to cast PDMS molds and B) after it had been used to cast seven PDMS molds. C, D) AFM images of PU replicas produced from different PDMS molds cast from this master.^[169]

AFM image of this gold master after it had been used to cast seven PDMS molds. We observed no damage to the gold master after its repeated use (ten times) to form PDMS stamps. Figures 19C and 19D show AFM images

of PU replicas generated from different PDMS molds. Again, we did not observe obvious change in the quality of these nanostructures on the PU replicas. These AFM images clearly demonstrate that this procedure is able to generate multiple copies of nanostructures starting from a single master. The simplicity and low cost of this procedure suggest its potential use in nanomanufacturing.

A modification of the procedure, replica molding against an PDMS mold while it is bent mechanically, allows the fabrication of nanostructures with feature sizes smaller than those on the original master.^[169] Figure 20A shows the AFM image of gold structures on another master with a feature size of about 50 nm, and Figure 20B the AFM image

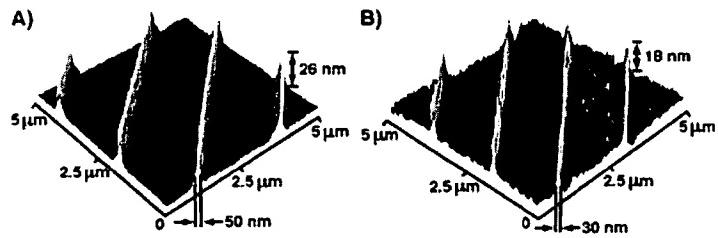


Figure 20. AFM images A) of Au structures on a master before it was used to cast PDMS molds and B) of a PU replica fabricated from a PDMS mold (cast from this master) while this mold was mechanically deformed by bending in a manner that generated narrower lines.^[169]

of a PU replica duplicated from a PDMS mold (cast from this gold master) while it was bent mechanically. The dimension of the features was reduced from 50 to 30 nm in this process.

The absence of techniques that are capable of generating and manufacturing nanostructures rapidly and economically represents one current limiting step in the area of nanoscience and nanotechnology.^[12] This work based on replica molding demonstrates a practical protocol for fabricating structures as small as approximately 30 nm in organic polymers, and with an accuracy in vertical dimension as small as about 5 nm. Recently, Chou et al. demonstrated a related procedure that might also be included in soft lithography: embossing or imprinting in organic polymers with rigid masters. This method generates features in thermoplastic polymers with dimensions as small as about 25 nm.^[18] Related work has also been demonstrated by groups at Phillips^[19a] and IBM.^[19b] These demonstrations make it clear that manufacturing (i.e., fabrication of multiple copies) of nanostructures of organic polymers is a practical reality. The ability to make both positive and negative polymeric replicas and to modify the dimensions and shapes of features present on elastomeric molds by mechanical deformation adds further flexibility to this methodology. Using nanostructures to generate electronically, optically, and magnetically functional components and systems will require the development of new technologies; the present work may provide one solution to the problem of mass production of nanostructures. Lessons learned from this process will be valuable in building more versatile systems.

4.1.2. Fabrication of Complex Optical Surfaces

Replica molding against a deformed PDMS mold provides a new strategy for making topologically complex structures and optically functional surfaces.^[35, 168] It allows the sizes and shapes of features present on the surface of the mold to be changed in a controlled way (by mechanical compression, bending, stretching, or a combination of these deformations) and generates complex structures from simple, regular structures on planar surfaces. The highly isotropic deformation of the PDMS mold even permits patterned microstructures to be formed with gradients in size and shape. The relief features on the PDMS mold are reconfigured by mechanical deformation, and the deformed structures are replicated by casting an UV-curable liquid PU or a thermally curable epoxy against it. The capability and feasibility of this procedure has been demonstrated by the production of^[35] 1) diffraction gratings with periods smaller than the original grating used as the master to cast the PDMS mold, 2) chirped, blazed diffraction gratings on planar and curved surfaces, 3) patterned microfeatures on the surfaces of approximately hemispherical objects, and 4) arrays of rhombic microlenses.

Figure 21 summarizes the typical procedures used in replica molding against elastomeric molds under mechanical deformation.^[35] Figure 21 A shows the procedure for replica molding against a PDMS mold under mechanical compression. If desired, this procedure can be repeated, using the PU replica as the starting point, to make structures more complex than

can be generated in one cycle (although with some degradation in the quality of the fabricated structures). Using a test structure of parallel lines, two cycles of compression and replication reduced the size of some features (that is, the recessed areas on the mold) from 1.6 μm to about 200 nm, and reduced the period of this test pattern from 3.6 to about 1.5 μm.^[35] Figure 21 B illustrates the procedure that we used to fabricate diffraction gratings on cylindrical surfaces. A thin PDMS mold (ca. 50 μm thick) was bent to make conformal contact with a curved surface coated with a thin film of liquid PU. After curing the PU, the PDMS mold was removed to reveal the PU replica on the surface of the cylindrical substrate. Figure 21 C shows a similar procedure that was used to produce an approximately hemispherical object having micropatterned relief structures on its surface. A thin PDMS mold (ca. 1 mm thick) was mounted across the end of a hollow glass tube and deformed by applying positive or negative pressure through the tube. The resulting curved surface was then replicated in PU.

By compressing one end of the elastomeric mold more than the other, it was straightforward to fabricate a chirped diffraction grating, a grating whose period changes continuously with position.^[172] More interestingly, the shape of the diffracting elements was largely preserved in this process: If we used a blazed grating as the starting master, the resulting chirped PU replica was also a blazed grating (Figure 22).^[35] The period (λ) of this chirped, blazed grating changed continuously from a value of about 1.55 to about 1.41 μm over a distance of approximately 0.9 cm; the rate of chirping $d\lambda/dz$ was approximately 1.6×10^{-5} . This grating was characterized in transmission at normal incidence. Figure 22 C shows the diffraction patterns (the zero-order and the two first-order peaks) of the PDMS mold, its PU replica, and the chirped PU grating. The first diffraction peak shifted continuously in position as the laser spot was scanned across the chirped grating along the z direction.

Figure 23 shows the SEM image of a hemispherical PU object with a pattern of corner cubes on its surface.^[35, 168] The shape of this polymeric object can be easily tuned by changing the thickness of the PDMS mold or the applied pressure or both. We have made a range of different patterns and relief structures; the smallest feature had a size of about 1.5 μm.

4.2. Microtransfer Molding

In microtransfer molding (μ TM, see Figure 17 B)^[36] a drop of liquid prepolymer is applied to the patterned surface of a PDMS mold and the excess liquid is removed by scraping with a flat PDMS block or by blowing off with a stream of nitrogen. The filled mold is then placed in contact with a substrate and irradiated or heated. After the liquid precursor has cured to a solid, the mold is peeled away carefully to leave a patterned microstructure on the surface of the substrate.

Figure 24 shows SEM images of typical structures of polymers that were fabricated by μ TM.^[36] Microtransfer molding is capable of generating both isolated and interconnected microstructures (Figure 24 A). The most significant advantage of μ TM over other microlithographic techniques is

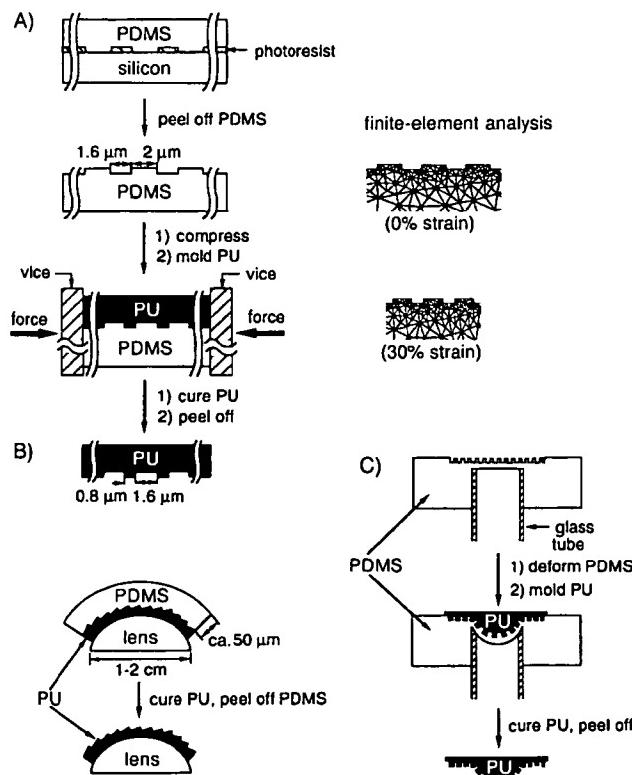


Figure 21. Schematic illustration of procedures for replica molding against elastomeric PDMS molds under A) mechanical compression, B) bending, and C) stretching.^[35] The reconfigured surfaces in PDMS are replicated with a UV-curable prepolymer of PU.

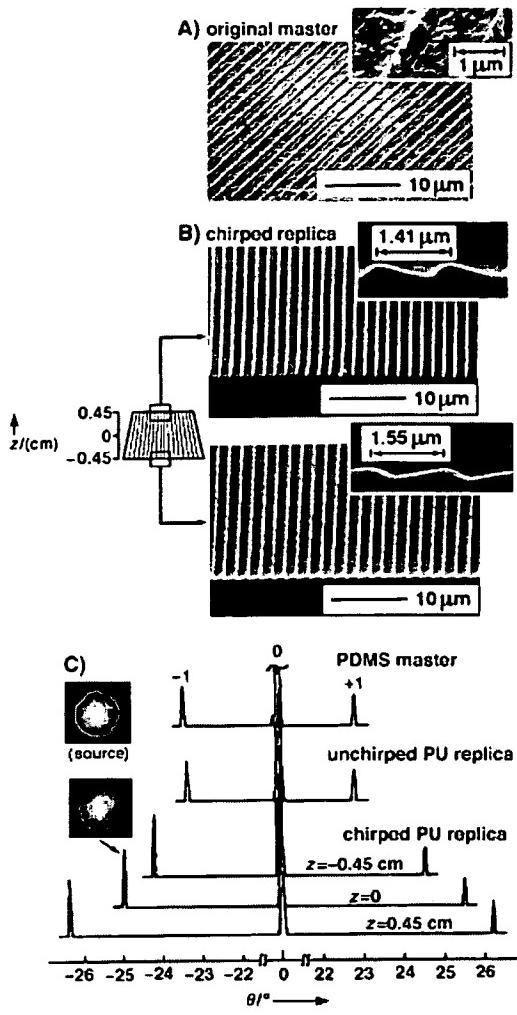


Figure 22. Cross-sectional SEM images of A) a commercial blazed diffraction grating and B) selective regions of a planar, chirped, blazed PU replica grating that was fabricated by molding against the PDMS mold while it was compressed asymmetrically. C) Diffraction patterns from the PDMS master, its PU replica, and the chirped PU grating. A He-Ne laser ($\lambda = 632.8 \text{ nm}$) was used.^[35]

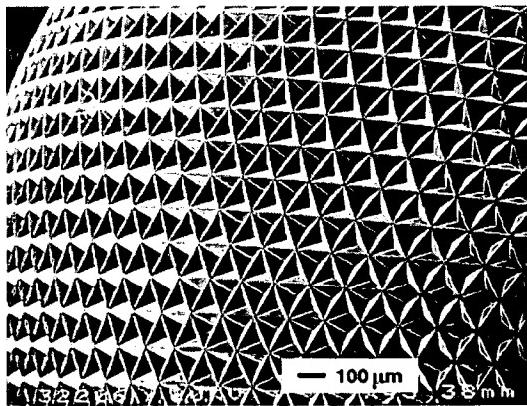


Figure 23. An SEM image of a dome-shaped object in polyurethane with patterned microstructures (corner cubes ca. 100 μm) on its surface that was formed by replica molding against a stretched PDMS mold.^[35]

the ease with which it can fabricate microstructures on nonplanar surfaces, a characteristic that is essential for building three-dimensional microstructures layer by layer.

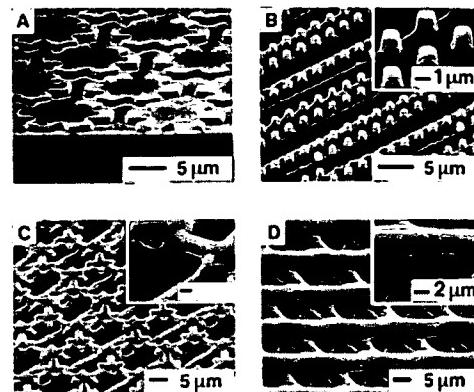


Figure 24. SEM images of polymeric microstructures fabricated by μTM :^[36] A) patterned, isolated microstructures of PU on silver (one layer); B) isolated microcylinders of epoxy on 5-μm lines of epoxy supported on a glass slide (two layers); C) a continuous web of epoxy over a layer of 5-μm lines of epoxy supported on a glass slide (two layers); D) a three-layer structure on a glass slide made from a thermally curable epoxy.

Figure 24B shows microposts of thermally curable epoxy fabricated on an array of parallel lines made of the same material. Figure 24C shows a continuous polymeric web fabricated over separated polymer lines. Figure 24D shows a three-layer structure of epoxy fabricated by μTM . Analogues of these two- and three-dimensional microstructures may find potential application in integrated optics,^[173] applied optics (as photonic crystals^[174]), and tissue engineering.^[175]

Microtransfer molding can generate microstructures over relatively large areas (ca. 3 cm^2) within a short period of time (ca. 10 min). It has been used to fabricate optical waveguides, couplers, and interferometers from organic polymers.^[176] We fabricated arrays of polymeric waveguides (both single- and multimode) of 3 cm in length from thermally curable epoxies and UV-curable PU; both polymers could be pristine or doped with fluorescent dyes (e.g. rhodamine 6G).^[36] An array of such waveguides could be turned into optical couplers and interferometers by tuning the separation between them; the coupling could also be controlled after fabrication by additional exposure to UV light.^[176] Microtransfer molding also has the capability of forming patterned microstructures of a wide variety of other materials. Figures 25A and 25B show SEM images of microstructures of glassy carbon (an interdigitated capacitor and an optical deflector, respectively); the structures were fabricated by μTM with a polymeric precursor (a phenolic resin modified with furfuryl alcohol) followed by pyrolysis at elevated temperatures.^[177] Figures 25C and 25D give SEM images of microstructures (an array of square pyramids and a free-standing membrane, respectively) of glasses fabricated from sol-gel precursors.^[178] One important shortcoming of μTM in its current state of development is that microstructures fabricated on a flat surface usually have a thin film (ca. 100 nm) between the raised features. This film prevents the underlying substrate from being attacked by chemical etchants, and must be removed by reactive-ion etching with O_2 if we want to use these patterned structures of polymers as masks to control the etching of the underlying substrate. Although removing this film requires a separate

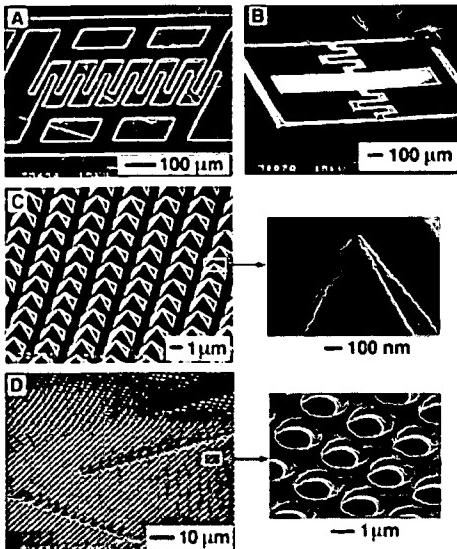


Figure 25. SEM images of A, B) microstructures of glassy carbon^[177] and C, D) glasses fabricated by μTM and molding.^[178] The retention of details in both procedures is very good.

step and is an inconvenience, we believe that μTM will find a broad application in microfabrication, especially for making three-dimensional microstructures.

4.3. Micromolding in Capillaries

Micromolding in capillaries (MIMIC) represents another non-photolithographic method that forms complex microstructures on both planar and curved surfaces.^[37] In MIMIC (see Figure 17C) the PDMS mold is placed on the surface of a substrate and makes conformal contact with that surface; the relief structure in the mold forms a network of empty channels. When a low-viscosity liquid prepolymer is placed at the open ends of the network of channels, the liquid spontaneously fills the channels by capillary action. After filling the channels and curing the prepolymer into a solid, the PDMS mold is removed, and a network of polymeric material remains on the surface of the substrate. A variety of materials (see Table 3) have been used in this process^[37] including prepolymers that are curable either with UV light or thermally,^[179] precursors to carbons^[177] or ceramics,^[180] structural and functional polymers,^[181, 182] polymer beads,^[183] colloids,^[184] inorganic salts,^[184] sol–gel materials,^[185] and biological macromolecules.^[186]

Microfabrication based on MIMIC is remarkable for its simplicity and its fidelity in transferring the patterns from the mold to the polymeric structures that it forms. MIMIC is applicable to patterning a broader range of materials than is photolithography. MIMIC forms patterned structures in a single step, and patterning structures with multiple thicknesses (quasi-three-dimensional structures) is possible. The smallest features that we produced using this procedure were parallel lines with cross-sectional dimensions of about $0.1 \times 2 \mu\text{m}^2$.^[179] These dimensions were set by the PDMS molds that were available for use with this work; we have not tried molds with smaller features, and therefore the lower limit to the pattern definition that can be achieved by this technique has not been established.

MIMIC does have several limitations: 1) It requires a hydraulically connected network of capillaries; it cannot, therefore, form isolated structures or patterns on contoured surfaces. 2) Although capillary filling over a short distance (ca. 1 cm) can be achieved quickly and efficiently, the rate of filling over a large distance decreases significantly due to the viscous drag of the fluid in the capillary. 3) Since the rate of filling is proportional to the cross-sectional dimension of the capillary, the extremely slow filling of small capillaries may limit the usefulness of MIMIC in certain types of nanofabrication. Nevertheless, several groups have demonstrated that appropriate liquids could wet and fill nanometer-sized capillaries over short distances.^[187, 188] 4) The forward ends of capillaries may fill incompletely if the hydraulic drag is sufficiently high.^[189] Interestingly, capillaries with closed ends may fill completely if they are short; the gas in them appears to escape by diffusing into the PDMS.

4.3.1. The Principle of MIMIC

Capillary filling is a very simple and well-known phenomenon,^[190] and the dynamics of wetting and spreading of liquids in capillaries has been studied systematically.^[190] The flow of a liquid in a capillary occurs because of a pressure difference between two hydraulically connected regions of the liquid mass, and the direction of flow decreases this difference in pressure. In circular capillaries, the flow of a wetting liquid occurs initially in thin films that wet the capillary symmetrically; in noncircular capillaries the most rapid flow usually occurs in the corner regions.^[191]

The rate of capillary filling is determined by the surface tension γ and viscosity η of the liquid, the radius of the capillary R , and the length of the filled section of the capillary z [Eq. (2); γ_{LV} , γ_{SV} , and γ_{SL} are liquid–vapor, solid–vapor, and solid–liquid interfacial free energies].^[190] The rate of filling

$$\frac{dz}{dt} = \frac{R\gamma_{LV}\cos\theta}{4\eta z} = \frac{R(\gamma_{SV} - \gamma_{SL})}{4\eta z} \quad (2)$$

is proportional to the cross-sectional dimension of the capillary as well as inversely proportional to the length of capillary that contains the liquid and to the viscosity of the liquid. The rate of filling decreases as the capillary fills or when a more viscous liquid is used.

The shape of the imbibition front strongly depends on the interfacial free energies. Kim et al. characterized the system and studied this relationship qualitatively using gold surfaces derivatized by SAMs of alkanethiolates terminated in different head groups (Figure 26).^[189] In agreement with Equation (2), the product of the length of filling and the rate of filling [$z(dz/dt)$] shows a linear dependence on the cosine of the advancing contact angles θ_a . The SEM images of the fronts (insets in Figure 26) indicate that different values of $\cos\theta_a$ result in different shapes of imbibing liquids: 1) For liquids with small advancing contact angles (Figure 26a, b) the imbibition fronts can be characterized as slipping films; 2) for liquids with intermediate advancing contact angles (Figure 26c, d) the shapes of the imbibition fronts consist of leading edges that suggest slipping films with shoulders; 3) for

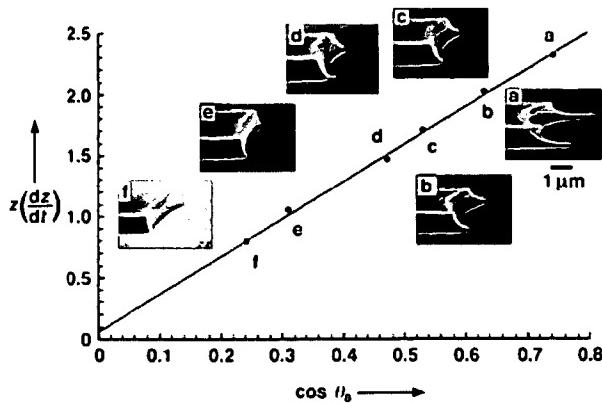


Figure 26. Dependence of the rate of capillary filling, represented by $z(dz/dt)$ in $10^4 \mu\text{m}^2\text{s}^{-1}$, and the imbibition shape (insets) on interfacial free energies of the surfaces^[189] as described with the the dynamic contact angle θ_0 between the liquid polymer and the SAM-derivatized surface.

liquids with high advancing contact angles (Figure 26 e, f) the bulk liquids flow as a whole without having precursor structures. The imbibition shapes can be described as wedge or bulk-flow.

4.3.2. MIMIC of Solventless Systems

The capability and feasibility of MIMIC have been demonstrated by the fabrication of patterned structures from a variety of liquid prepolymers: PU, polyacrylates, and epoxies.^[37, 179] These prepolymers have a shrinkage of less than 3% after curing.^[171] The cured polymers, therefore, possess almost the exact dimensions and shapes of the channels in the surface of the PDMS mold; they can be directly used as masks in the etching of the underlying substrates. Figure 27 shows SEM images of polymeric microstructures that were fabricated by MIMIC. The polymer

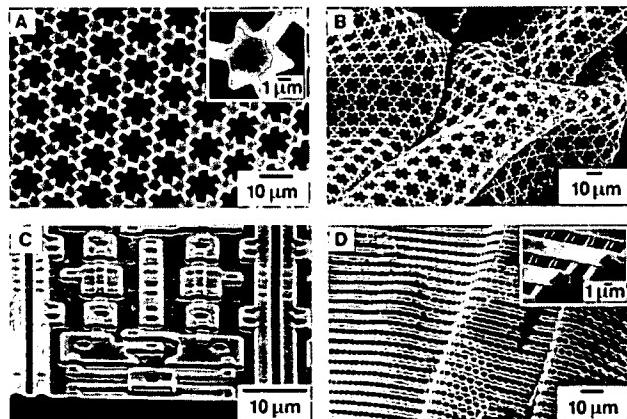


Figure 27. SEM images of polymeric microstructures fabricated by MIMIC from prepolymer of polyacrylate (A, C) and polyurethane (B, D) without solvents.^[37, 179] The structures in B and D are freestanding; the buckling occurred during sample preparation and demonstrated their strength.

microstructure could be freed from the support by dissolving a sacrificial layer of glass or SiO_2 in an aqueous solution of $\text{HF}/\text{NH}_4\text{F}$ (Figure 27B).^[37] MIMIC also allows quasi-three-dimensional processing (i.e., patterning layers with different

thicknesses) in a single step (Figure 27C).^[179] Such complex arrays of micro and submicrometer scale channels filled completely; in some regions of these structures, features are connected to one another by channels with thicknesses of less than 100 nm. The support used in MIMIC could have relief patterns on its own surface. Figure 27D shows the SEM image of a free-standing microstructure of PU that was formed between two PDMS molds.^[37, 179] Each PDMS mold has a relief pattern of parallel lines on its own surface. After the filling with liquid prepolymer and the curing of the prepolymer into a solid, the two PDMS molds were separated. The cross-linked polymeric microstructure remained on the surface of one of the two PDMS molds and could be easily released. These two layers of polymeric lines formed *one* interconnected polymeric microstructure. This type of free-standing microstructure, two layers with an independent relief structure in each, cannot be fabricated by photolithography.^[10]

4.3.3. MIMIC of Systems with Solvents

Although MIMIC was developed based on prepolymers having no solvents, it has also been extended to those systems where solvents are involved.^[182–186] The solvents were evaporated after the solutions had filled the channels. The only requirement seems to be that the solvent does not swell PDMS. It has been extremely difficult (or impossible) to fabricate patterned structures of those materials such as polymer beads (Figure 28 A, B) and ceramics (Figure 28 E, F)

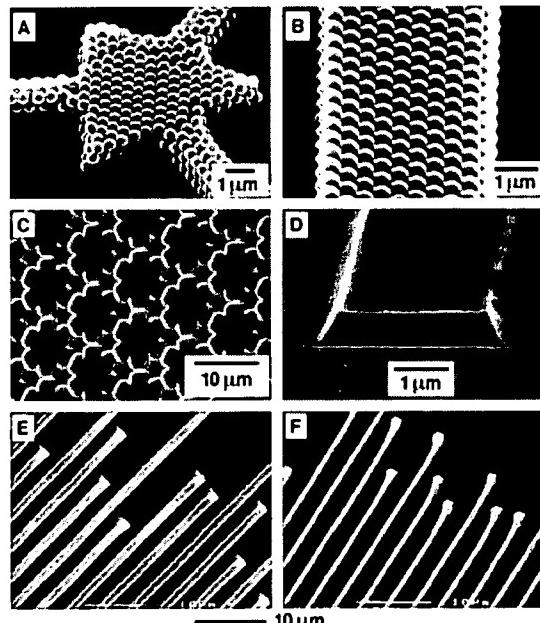


Figure 28. SEM images of patterned microstructures of A, B) polymer beads,^[183] C, D) polyaniline emeraldine HCl salt,^[182] and E, F) zirconium oxide^[180] fabricated by MIMIC from their solutions in water, *N*-methyl-2-pyrrolidone, and ethanol, respectively. The crystallization of the polymer beads occurred spontaneously. The structures of polyaniline were molded from a solution of polyaniline emeraldine base in *N*-methyl-2-pyrrolidone, and then converted into the conductive form of emeraldine salt by doping in aqueous HCl. The zirconium oxide was formed from a precursor polymer that has been molded into the structure shown in E. The precursor polymer was obtained from Chemat Technology (ZO9303), and was converted into ZrO_2 by heating at about 600°C for 10 h. The ends of the lines deadhered from the substrate during thermal conversion.

with photolithography. Figure 28 shows SEM images of some patterned microstructures that were fabricated by MIMIC from systems involving solvents or suspending liquids. The ability to form patterned microstructures offers new opportunities for these materials. For example, the closely packed, multilayered structures of polymer beads are interesting for potential applications in chromatography and diffractive optics.^[192] The ability to form patterned microstructures of conducting polymers provides a potential route to flexible, all-plastic electronic and optoelectronic devices.^[193]

4.3.4. Fabrication of Functional Microelectronic Devices

Nuzzo et al. fabricated ferroelectric capacitors made up of thin films of Pt/Pb(Zr,Ti)O₃/Pt by μCP and selective CVD.^[194] Recently Hu, Jeon et al. used MIMIC successfully to fabricate simple, electrically functional devices.^[195–197] They demonstrated the fabrication of Schottky diodes,^[195] GaAs/AlGaAs heterostructure field effect transistors (FETs),^[196] and silicon metal oxide semiconductor FETs (MOSFETs).^[197] The fabrication process for both types of transistors required at least three MIMIC steps and two registration steps. Figure 29 outlines the fabrication of the GaAs/AlGaAs heterostructure FET.^[196] Figure 30 A shows the oblique view of the device. The source and drain are AuNiGe ohmic contacts, the channel is defined by a mesa etch, and the gate is a Cr/Au Schottky contact. In each step the pattern was defined by microstructures of PU formed by MIMIC (see Figure 29): Etching and evaporation were performed using these PU structures as the masks. Figure 30 B shows an optical micrograph of the FET, and Figure 30 C the performance of a representative GaAs/AlGaAs FET fabricated by this procedure. Its characteristics are similar to those of GaAs/AlGaAs FETs made using conventional photolithographic techniques as the patterning tools. The fabrication of the Si MOSFETs followed a similar procedure, but used PU microstructures to form the mask layers used during implantation of the silicon.^[197] Although the feature sizes (16–26 μm) that characterize these devices are about 100 larger than those of state-of-the-art commercial devices (ca. 250 nm), these results established that soft lithography is compatible with the multilayer fabrication that has, up to now, been monopolized by photolithography and set a benchmark against which to measure further developments in this area.

4.4. Solvent-Assisted Micromolding

Solvent-assisted micromolding (SAMIM) is a technique that allows fabrication of patterned, quasi-three-dimensional microstructures on the surfaces of polymeric substrates.^[38] It can also be used to modify surface morphologies of polymers. The operational principle of this technique shares characteristics with both replica molding and embossing (see Figure 17D). An elastomeric PDMS mold is wetted with a solvent that is a good solvent for the polymer, and is brought into contact with the surface of the polymer. The solvent dissolves (or swells) a thin layer of the polymer, and the resulting (probably gellike) fluid comprising polymer and

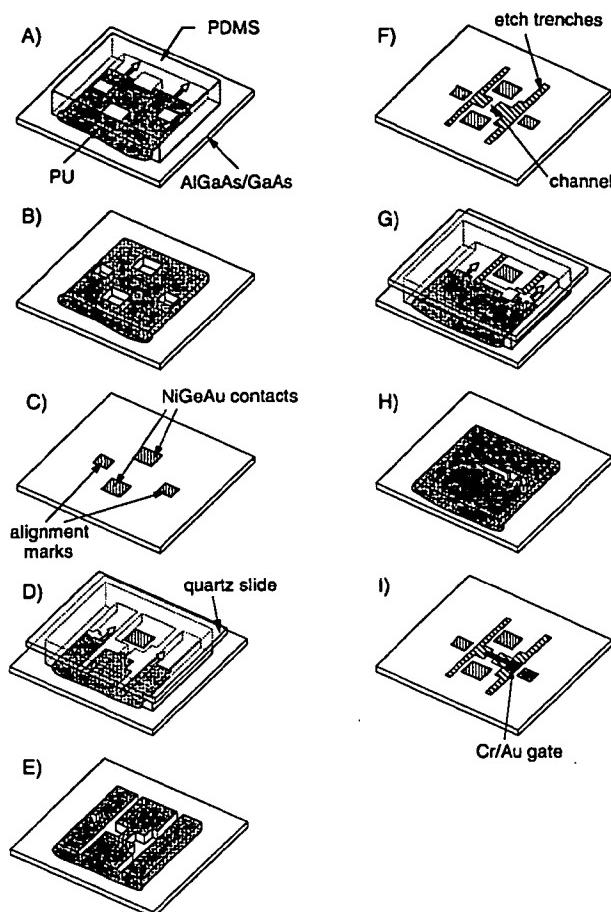


Figure 29. Schematic illustration of the procedure for the fabrication of GaAs/AlGaAs FETs.^[196] A) Use MIMIC to define ohmic contacts and alignment marks. B) Cure PU, peel off the PDMS mold, and remove the thin film of PU adjoining the microstructures. C) Evaporate AuNiGe, lift off PU, anneal to form ohmic contacts for the source, and drain. D) Register and use MIMIC with another PDMS mold to define etch trenches. E) Cure PU, peel off the PDMS mold, and remove the connecting film of PU. F) Etch in an aqueous solution of citric acid and hydrogen peroxide to remove the 2DEG in the etched trenches. G) Register and use MIMIC with a third PDMS mold to define the gate. H) Cure PU, peel off the PDMS mold, and remove the thin film of PU. I) Evaporate Cr/Au and lift off PU to form the gate.

solvent conforms to the surface topology of the mold. While the mold is maintained in conformal contact with the substrate, the polymer solidifies as the solvent dissipates and evaporates (probably by diffusion through the mold) to form relief structures with a pattern complementary to that on the surface of the mold.

SAMIM is an experimentally simple procedure. The key elements are wetting of the PDMS mold by a liquid that is a solvent for the polymer to be molded and conformal contact between the solvent-coated elastomeric mold and the substrate. The choice of solvent for a polymer determines the effectiveness and success of SAMIM. The solvent should rapidly dissolve or swell the surface of the polymer; it should not, however, swell the PDMS mold and thereby distort the mold and/or destroy the conformal contact between the polymer and the mold.^[126] In general, the solvent should have a relatively high vapor pressure and a moderately high surface tension (e.g., methanol, ethanol, and acetone) to ensure rapid

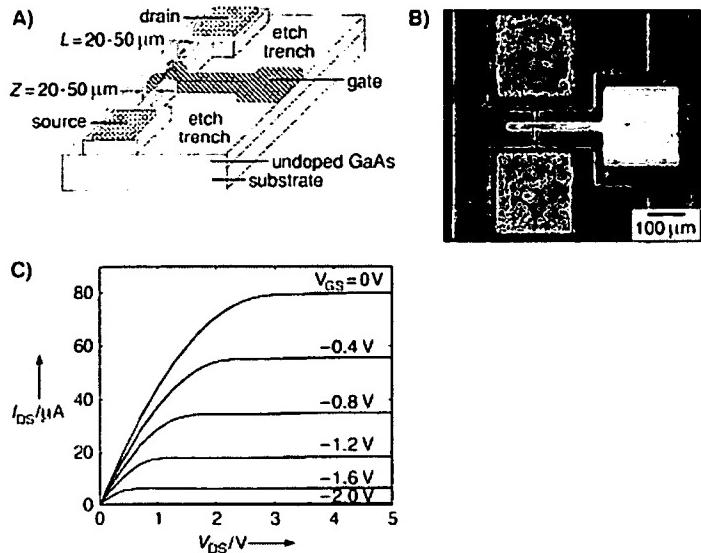


Figure 30. A) Schematic diagram of a GaAs/AlGaAs FET. B) Optical micrograph of a GaAs/AlGaAs FET fabricated by MIMIC (gate length $L = 26 \mu\text{m}$, gate width $Z = 16 \mu\text{m}$).^[196] C) The performance of a representative GaAs/AlGaAs FET fabricated by this procedure.^[196] I_{DS} = current between drain and source, V_{DS} = voltage between drain and source, V_{GS} = voltage between gate and source.

evaporation of the excess solvent and minimal swelling of the PDMS mold. Dyes and inorganic salts can also be added to the solvent; they are subsequently incorporated into the resulting microstructures. Solvents with low vapor pressures (e.g., ethylene glycol and dimethyl sulfoxide) are not well suited for SAMIM. Surface modification^[122] of the PDMS mold may be required when solvents with high surface tensions are used since they only partially wet the PDMS surface. Many nonpolar solvents (e.g., toluene and dichloromethane) cannot be used in SAMIM because they can swell the PDMS mold.

Replication of patterns with complex topology is practical in a single step by SAMIM. This procedure is also suitable for forming patterned relief microstructures over a large area and is applicable to a variety of polymers when appropriate solvents are selected, for example, ethanol or 2-propanol for Microposit photoresists (a phenol-formaldehyde resin) or acetone for polystyrene, poly(methyl methacrylate), cellulose acetate, and poly(acrylonitrile-butadiene-styrene). Figure 31 A shows the SEM image of patterned relief structures formed on a polystyrene film with acetone as the solvent.^[38] These quasi-three-dimensional features are well defined and clearly resolved. A common characteristic of patterned microstructures generated by SAMIM is that the resulting structures are adjoined by a thin film of the polymer. These films can sometimes be removed by homogeneous thinning by reactive-ion etching with O_2 . Figure 31 B shows AFM images of the smallest features that we have generated in a thin film of photoresist by SAMIM with ethanol as the solvent: parallel lines that are about 60 nm in width and about 50 nm in height.^[38]

SAMIM can generate quasi-three-dimensional microstructures or morphologies on the surface of a polymer using a solvent that can soften the polymer without affecting the PDMS mold. SAMIM differs from other existing techniques

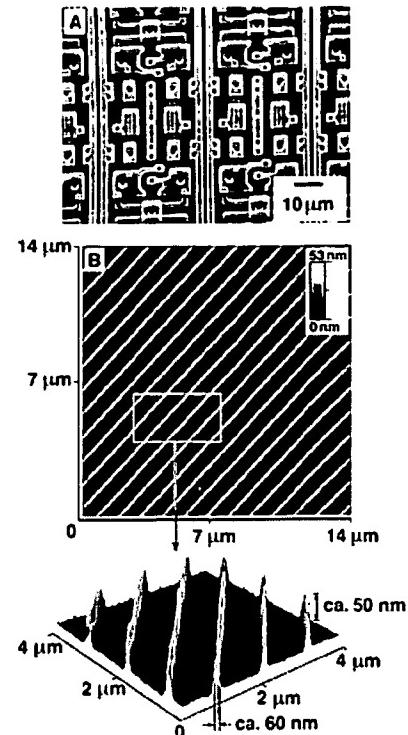


Figure 31. A) SEM and B) AFM images of polymeric microstructures fabricated by SAMIM.^[38] The polymers used here were thin films (A: ca. $1.6 \mu\text{m}$ thick; B: ca. $0.4 \mu\text{m}$ thick) of a photoresist (Microposit 1805, Shipley) that was spin-coated on Si wafers. The solvent was ethanol.

(e.g., embossing with a rigid master^[18] or MIMIC) in several ways. First, it uses an elastomeric rather than a rigid mold. Second, it uses a solvent instead of increased temperatures to “soften” the surface of the polymer. The process is simple, rapid, and does not require specialized equipment or a system for pressing the mold into the substrate. Third, it does not suffer from slow rates of capillary filling, which limits MIMIC to relatively small areas; it is also not restricted to fabrication of hydraulically connected structures. Fourth, it can be used with a wide range of polymers or prepolymers: the only requirement seems to be a solvent that dissolves the polymer of the substrate and wets the surface of the PDMS mold but does not significantly swell the mold.

5. Summary and Outlook

As fabrication of microstructures grows in importance in a wide range of areas—from microelectronics through optics, microanalysis, combinatorial synthesis, display, and MEMS to cell biology—the utility of new methods for patterning will certainly increase. The techniques of soft lithography—self-assembly, contact printing, micromolding, and contact phase-shift photolithography^[115]—illustrate the potential for application of the largely unexplored, non-photolithographic procedures for micro- and nanofabrication to these new areas.

Soft lithography offers immediate advantages (Table 8) in applications in which photolithography clearly falters or fails: For example, manufacturing below the scale of 100 nm, patterning on nonplanar surfaces, fabrication of three-dimensional structures, patterning of functional materials other than

Table 8. Advantages and disadvantages of soft lithography.

Advantages

- convenient, inexpensive, accessible to chemists, biologists, and material scientists
- basis in self-assembly tends to minimize certain types of defects
- many soft lithographic processes are additive and minimize waste of materials
- readily adapted to rapid prototyping for feature sizes $> 20 \mu\text{m}$
- isotropic mechanical deformation of PDMS mold or stamp provides routes to complex patterns
- no diffraction limit; features as small as 30 nm have been fabricated
- nonplanar surfaces (lenses, optical fibers, and capillaries) can be used as substrates
- generation and replication of three-dimensional topologies or structures are possible
- optical transparency of the mask allows through-mask registration and processing
- good control over surface chemistry, very useful for interfacial engineering
- a broad range of materials can be used: functional polymers, sol-gel materials, colloidal materials, suspensions, solutions of salts, and precursors to carbon materials, glasses, and ceramics
- applicable to manufacturing: production of indistinguishable copies at low cost
- applicable in patterning large areas

Disadvantages and Problems

- patterns in the stamp or mold may distort due to the deformation (pairing, sagging, swelling, and shrinking) of the elastomer used
- difficulty in achieving accurate registration with elastomers ($< 1 \mu\text{m}$)
- compatibility with current integrate-circuit processes and materials must be demonstrated
- defect levels higher than for photolithography
- μCP works well with only a limited range of surfaces; MIMIC is slow; REM, μTM , and SAMIM leave a thin film of polymer over the surface

photoresists, and modification of surfaces. Figure 32 summarizes the current state of development of soft lithography as well areas in which its potential is particularly clear. Most work in soft lithography has concentrated on single-step processing; our recent successes in multilayer fabrication requiring registration (albeit with features of about 20 μm) has established a modest potential in multilayer structures and functional microelectronic devices.^[194-197] This demonstration paves the way for the evaluation of soft lithographic techniques in microelectronics, although serious technological use will require substantial further development.

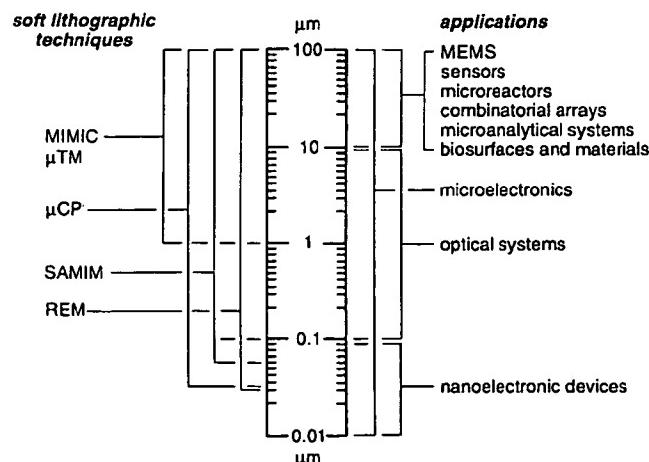


Figure 32. Summary of the current state of development of soft lithographic techniques and areas in which these techniques find applications.

Photolithography will of course continue as the dominant technology in microfabrication of technologically sophisticated semiconductor devices and systems for the foreseeable future. There are, however, many existing and emerging uses for soft lithography that take advantage of (or require) the characteristics of these techniques. Soft lithographic materials offer experimental simplicity and flexibility in forming certain types of patterns. Procedures involving relatively large features ($> 1 \mu\text{m}$) can be conducted in an unprotected laboratory environment, and thus are especially useful in laboratories that do not have routine access to the facilities normally used in microfabrication, or for which the capital cost of equipment is a serious concern. At the current state of development, they can replace photolithographic techniques in many problems of microfabrication where requirements for precise alignment, continuity, isolation, and uniformity in the final patterns are relaxed: for example, production of single-level structures for use in microelectrode arrays, sensors, biosensors, and microanalytical systems. Simple display devices, optical components, and elementary microelectronic devices also now seem practical. The initial success of soft lithography also suggests that it will be useful to reexamine other relatively undeveloped patterning techniques (see Table 2) for their potential for application in emerging technologies or in high-resolution patterning.

A number of issues remain to be solved before soft lithography invades the core applications of photolithography, that is, those in microelectronics. First, high-resolution ($\leq 20 \text{ nm}$) registration with elastomeric materials must be demonstrated. The distortion and deformation associated with elastomeric materials must also be managed, and pattern transfer must be made exactly reproducible. Second, the quality of the patterns and structures produced must be improved. These patterns, especially for narrow lines, are not yet compatible with the levels of quality required for microfabrication of complex electronic devices. The formation and distribution of defects in SAMs, and especially their influence on the quality of patterns formed when they are used as resists for etching, must be understood and improved. Third, the compatibility of these patterning techniques with the range of processes used in the production of microelectronic circuitry must be explored. In particular, systems that form SAMs directly on semiconductors and are optimized for compatibility with current processes (especially etching with reactive ions) and materials are required.

Researchers and manufacturers of microstructures have specific requirements of any microlithographic technology: flexibility during the development process; reproducibility, reliability, and simplicity during manufacturing; and cost-effectiveness for commercial success. Judged against these standards, soft lithography has the potential to become an important addition to the field of micro- and nanofabrication, although it is still in an early stage of technical development.

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Unconventional Methods for Fabricating and Patterning Nanostructures

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1. Introduction

Fascinating (and sometimes technologically important) phenomena occur in systems that have a spatial dimension comparable to that of a fundamental physical, chemical, or biological process. Some of the most interesting examples—ballistic movement of an electron in a semiconductor,¹ near- and far-field diffraction of visible light,² diffusion of an active species close to an electrode,³ excitation of a collective

resonance by light,⁴ attachment or spreading of a eukaryotic cell^{5–7}—can be observed in structures that have dimensions larger than macromolecules (~2–20 nm) but smaller than or equal to eukaryotic cells (~1–50 μm). Structures with these dimensions are often referred to as meso-scale systems or “mesosystems”.^{8,9} Because mesosystems bridge the molecular and the macroscopic world, fabrication and study of these systems have become active areas of research in physics, materials science, and increasingly in chemistry and biology. Nanosystems—systems that we define as having features or characteristic lengths between 1 and 100 nm—exhibit particularly peculiar and interesting characteristics: quantized excitation,^{10,11} Coulomb blockade,¹² single-electron tunneling (SET),¹³ and metal–insulator transition.¹⁴ These phenomena occur in structures small enough for quantum mechanical effects to dominate. Other interesting physical processes that can be observed in similar structures—for example, near-field optical behavior^{15,16} and interaction of light with photonic band-gap crystals¹⁷—represent nanoscopic manifestations of processes that have more familiar macroscopic analogues (in these two cases, interaction of microwave radiation with antennas or apertures¹⁸ and operation of microwave band-gap structures¹⁹). The fundamental study of phenomena that occur in structures having dimensions in the 1–100 nm regime has already evolved into a new field of research that is sometimes referred to as nanoscience.^{20–23}

In addition to their uses in nanoscience, nanostructures are central to the development of a number of existing and emerging technologies. The ability to fabricate on the nanometer scale guarantees a continuation in the miniaturization of functional devices. In microelectronics, “smaller” has always meant better—more components per chip, faster response, lower cost, lower power consumption, and higher performance.^{24–26} The miniaturization and production of microelectronic chips has, in recent years, been guided by a road map issued by the Semiconductor Industry Association (SIA). The current SIA road map forecasts a steady downward trend in the minimum feature size of DRAMs from ~250 nm today to ~70 nm in the year 2010.²⁷ Miniaturization may also be the trend in a range of other technologies. There are active efforts, for example, to develop magnetic storage media having elements with dimensions as small as ~100 nm,²⁸ compact disks (CDs) with pit sizes of <50 nm (to be read by scanning

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probe devices,²⁹ and nanometer-sized sensors or nanoelectromechanical systems (NEMS).³⁰ The ability to fabricate on the nanometer scale also allows for technologies that rely on physical principles (for example, quantum size effects) that cannot be exploited or are absent in macroscopic or microscopic structures. Revolutionary devices such as arrays of quantum dot lasers,³¹ quantum cascade lasers,³² single-electron transistors,³³ and arrays of nanometer-sized magnets³⁴ are appearing rapidly in prototype forms in research labs. Organic self-assembled monolayers have been used as a gate insulator in a nano-field effect transistors.³⁵



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There are also applications of nanostructures in areas that have not, so far, been seriously explored. For example, ultrasmall sensors or electrodes might be used to communicate with cells and to form the basis for minimally invasive diagnostic systems;³⁶ nanoscale chemical reactors and analytical probes could make the study of individual molecules routine;³⁷ and arrays of very large numbers of nanometer-scale systems could open the door to the study of statistical phenomena such as nucleation.

In almost all applications of nanostructures, fabrication represents the first and one of the most significant challenges to their realization. This review outlines a range of techniques that are, in principle, suitable for the fabrication of structures for applications in nanoscience and nanotechnology. The focus of the review is on new methods for replication of nanostructures based on printing, molding, or embossing,³⁸ and on methods that involve relatively inexpensive forms of near-field photolithography³⁹ or that use molecular self-assembly⁴⁰—rather than on extensions of projection photolithography (using ei-

ther EUV or X-ray photons) and electron- or ion-beam lithography⁴¹—for three reasons. First, we believe that these methods are less developed than conventional photo-, electron-, or ion-beam lithography and, hence, offer more opportunity for innovation. Second, there is more chemical and materials content to these methods, and they are more relevant to the interests of a chemical audience. Third, X-ray or EUV photolithography, e-beam, and focused ion-beam writing are technologies that are now well into advanced engineering development, and although there are important chemical/materials opportunities in all of them (for example, in developing advanced resists, in production and maintenance of masks, and in new materials for functional components of nanostructures), it will, in practice, be difficult for chemistry or materials science to influence significantly the outcome of these programs.

We define techniques for nanofabrication as those capable of generating structures with at least one lateral dimension between 1 and 100 nm;⁴² we will, however, also discuss a limited number of methods that, so far, have only been demonstrated at the ~200 nm scale but that we judge to have the potential to be improved to ≤100 nm. We devote the most attention to systems that can draw arbitrary or semiarbitrary patterns but we also outline ideas, like those based on self-assembly,⁴⁰ that may lead to useful regular arrays or that may be parts of systems capable of forming complex patterns. In general, we do not deal with structures such as zeolites (which have nanometer-scale dimensions⁴³ but limited potential for patterning) and only touch on structures such as carbon nanotubes (which have intensely interesting properties but which can, at present, only be grown, cut, and assembled, rather than patterned). Also, although many thin film structures, such as Langmuir–Blodgett (LB) films,⁴⁴ self-assembled monolayers (SAMs),^{45,46} and evaporated thin films have nanometer thicknesses and subnanometer internal structures, these films only represent structure out of the plane of the substrate. This review deals only with in-plane nanostructures.

We broadly divide the problem of fabrication of nanostructures (or nanolithography) into two separate parts: *writing* and *replication*.^{42,47} Writing and replication are usually different kinds of processes with different characteristics, and they also emphasize different aspects of nanofabrication. They both connect to the idea of a *master*: that is, a structure that provides or encodes a pattern to be replicated in multiple copies. *Writing* nanostructures or “making masters” is usually done by serial techniques such as writing with a focused beam of electrons or ions. *Replication* of nanostructures is a process of pattern transfer in which the information—for example, the shape, morphology, structure, and pattern—present on a master is transferred to a functional material in a single step, rapidly, inexpensively, and with high fidelity. Most techniques used for writing nanostructures *de novo* are either too slow or too expensive to be used for mass production. Replication of a master should provide an economical and convenient route to multiple copies of the nanostructures written on

the master. A combination of high-precision writing of masters with low-cost replication of these masters seems to provide the most practical protocol for nanomanufacturing: high-resolution, high-cost fabrication techniques can be used to make masters in one set of materials; these structures can then be replicated in a low-cost process in other materials. The cost of the master can be an insignificant part of the overall cost structure if it is used to make many replicas.

We begin this review with an overview of strategies that have been explored for fabricating patterned nanostructures. We then describe these strategies in detail in four sections: (i) current technologies with broad flexibility in patterning; (ii) new methods that have the potential for broad flexibility in patterning; (iii) techniques for making regular or simple patterns; and (iv) new concepts not yet demonstrated for nanometer-scale patterning but with long-term potential in nanotechnology.

2. Strategies for Fabricating Patterned Nanostructures

Table 1 summarizes strategies that have been explored for fabricating patterned nanostructures. These strategies include (i) lithography with photons, particles, and scanning probes; (ii) replication against masters (or molds) via physical contact; (iii) self-assembly; (iv) templated deposition; and (v) size reduction. Because many of these methods have only emerged recently, most of their characteristics—fidelity, resolution, density of errors, speed, and cost—are only vaguely known. We therefore emphasize their demonstrated performance (that is, feature size and flexibility in materials that can be patterned) and comment on their intrinsic limits (that is, limits that originate in the physics and chemistry on which they are based). In some cases, we highlight approaches that may circumvent shortcomings associated with the current forms of these techniques.

2.1. Lithography with Photons, Particles, and Scanning Probes

Photolithographic methods all share the same operational principle:^{48,49} exposure of an appropriate material to electromagnetic radiation (UV, DUV, EUV, or X-ray) introduces a latent image (usually a difference in solubility) into the material as a result of a set of chemical changes in its molecular structure; this latent image is subsequently developed into relief structures through etching. Methods based on writing with particles (electrons or ions) usually accomplish the same task using a scanned beam or projected image of energetic particles rather than photons. Exposure is usually patterned either by interposing a mask between the source of radiation (or particles) and the material or by scanning a focused spot of the source across the surface of the material. When masks are used, the lithographic process yields a replica (perhaps reduced in size) of the pattern on the mask. With scanning probes, a sharp tip induces local change in a resist or causes local deposition. Methods that involve scanning or

Table 1. Strategies and Intrinsic Limitations

pattern formation using ^a	basis for intrinsic limitations	strategies to circumvent the limitations
photons UV, DUV, EUV, and X-rays	diffraction depth of focus	contact mode, near-field exposure nonlinear photoresists
particles electrons and ions	electrostatic interactions writing is serial small field of writing de Broglie wavelength	neutral atoms projection arrays of sources
neutral atoms		
machining AFM, STM, NSOM, and electrochemical		
physical contact printing, molding, and embossing	writing is serial small field of writing van der Waals forces speed of capillary filling adhesion of mold and replica control over order, domain size, and density of defects	arrays of probes low-viscosity solutions surface modification
self-assembly surfactant systems block copolymers crystallization of proteins and colloids		
deposition cleaved edge overgrowth shadowed evaporation	low flexibility in patterning and fabrication of masks or templates	
size reduction glass drawing compression of elastomeric masters or molds controlled reactive spreading		low flexibility in patterning; reproducibility
edge-based technologies near-field phase-shifting photolithography topographically directed photolithography topographically directed etching	diffraction diffraction	

^a Abbreviations: UV (ultraviolet), DUV (deep ultraviolet), EUV (extreme ultraviolet); AFM (atomic force microscope); STM (scanning tunneling microscope); and NSOM (near-field scanning optical microscope).

writing can generate arbitrary patterns and therefore be used for master writing.

Pattern Formation Using Photons. Photons have been used for many years to induce chemical reactions in photographic materials⁵⁰ or resist polymers.⁵¹ The lithographic technology—photolithography—based on this process uses a mask or aperture to localize the photochemistry spatially; it is an invaluable tool for microfabrication in a broad range of applications in science and technology and one of the most widely used and highly developed of all technologies now practiced.⁴⁸ Although a scanned aperture (or a stationary aperture and a scanned sample) can be used to write arbitrary patterns, the predominant use of photolithography is to replicate a pattern on a mask into a layer of photoresist. In this case, the image of the mask is reduced (usually by a factor of 4) and projected onto the resist with an optical system (projection mode photolithography) or the mask is placed in physical contact with the resist (contact mode photolithography). Most fabrication in the integrated circuit (IC) industry uses projection-mode lithography; feature sizes of 250 nm with 248 nm UV light are common for fabrication in microelectronics.

The resolution of photolithography increases as the wavelength of the light used for exposure decreases. With 193 nm light from an ArF excimer laser and synthetic fused silica (or calcium fluoride) lenses, projection photolithography may yield a reliable (and perhaps economical) solution to patterning features as small as ~150 nm.^{52–54} Similar systems based on transmission optics with exposure wavelengths below

193 nm are difficult to construct, however, because of the lack of transparent materials suitable for lenses at these short wavelengths. One of the several technical challenges to extending photolithographic methods into the sub-100-nm range is, therefore, the development of reflection optics or stencil masks that can be used with very short wavelengths (for example, EUV with $\lambda \approx 0.2\text{--}100$ nm or soft X-rays with $\lambda \approx 0.2\text{--}40$ nm).^{55,56} Although lithography was demonstrated with soft EUV and X-rays many years ago, fabricating the masks and optics capable of supporting a robust, economical method still provides significant unsolved challenges.⁵⁷ Other, equally significant, problems include repairing the mask, limiting damage and distortion of the mask on exposure to high fluxes of energetic radiation, and achieving the registration required for multilevel fabrication. Controlling the capital cost of new facilities is also a key economic problem.

In addition to advances in the physics and engineering of new light sources and projection optics, clever designs for the chemistries of the photoresist have been critical to the success of photolithography. Chemically amplified resists^{51,58} and those based on surface silylation and dry development,⁵⁹ for example, have remarkably improved the speed of patterning and the fidelity of the transfer of patterns of intensity into the resist. Materials for antireflective coatings have been useful as well.⁴⁹ Also, when operated in the linear response regime, photoresists can be used to image distributions of intensity^{60,61} and can guide the optical design of new types of photolithographic systems. By exploiting the nonlinear response of

conventional resists, it is even possible to produce patterns that have features smaller than or geometries different from those present in the linear optical image.^{62,63} Special classes of nonlinear resists, such as those based on two-photon absorption, are specifically designed to produce well-defined nonlinearities that can be used to increase the resolution.⁶⁴ Although these nonlinear resists are not applicable to general tasks in nanopatterning (for example, they cannot generate densely packed features), they may be important for specialized applications. Other key technologies in IC processing such as reactive ion etching (RIE),⁶⁵ lift-off,⁴⁸ deposition,⁴⁸ ion implantation,⁶⁶ and planarization of wafers⁶⁷ also contain important chemical and materials components that could, potentially, be improved to deliver or facilitate patterning of features below 100 nm.

Pattern Formation Using Particles. Energetic particles—electrons, ions, and electrically neutral metastable atoms—can also be used to form patterns with nanometer resolution in appropriate resist films; these approaches are attractive, in part, because the de Broglie wavelengths of these particles are sufficiently short (<0.1 nm) that they minimize the effects of diffraction that currently limit many photolithographic approaches. These methods can provide resolution higher than that required by the IC industry for the foreseeable future.⁴² For example, resolution of ~10 nm, which was achieved more than 20 years ago with e-beam writing,⁶⁸ comfortably exceeds the lithographic requirements necessary for the 50-nm technology projected for the year 2012.²⁷ Conventional lithography with focused beams of electrons or ions is, however, performed serially and is slow. For example, typical electron-beam patterning of a 4-in. wafer that has a high density of features requires ~1 h.⁶⁹ One means to increase the speed is to use stencil masks⁷⁰ and projection optics to expose large areas at once.⁷¹ These approaches appear promising: 80-nm features can now be routinely produced using a 4× reduction projection system for electrons.⁶⁹ It may also be possible to use large arrays of particle beams from single⁷² or multiple sources⁷³ to allow multiple serial writing processes to happen simultaneously. Even if these new approaches do not yield high-throughput solutions, it is certain that conventional lithography with focused beams of electrons and ions will remain indispensable tools for generating and repairing masks or masters with nanometer features for the foreseeable future.

Neutral metastable atoms can also be used for particle-based lithography. Neutral atoms are attractive partly because they do not electrostatically interact with one another. Their neutrality requires, however, development of new types of optics based on light forces if they are to be used with projection systems. Initial results are encouraging: features as small as ~50 nm have been fabricated in a single step over large areas with stencil masks,^{74,75} and ~70-nm features have been produced using directed deposition with light force lenses.^{76,77}

Pattern Formation Using Scanning Probes. Scanning probe lithography (SPL) encompasses techniques that use small (<50 nm) tips scanned near

the surface of a sample in the configuration of scanning tunneling microscopes (STMs),⁷⁸ atomic force microscopes (AFMs),⁷⁹ scanning electrochemical microscopes (SECM),⁸⁰ or near-field scanning optical microscopes (NSOMs).¹⁵ Although scanning probes were originally designed to provide high-resolution images of surfaces, their lithographic capability was demonstrated in a set of experiments with an STM, just five years after the first STM images were recorded.⁸¹ In that work, a large electrical bias applied between a tungsten tip and a germanium surface caused transfer of a single atom from the tip to the surface. Since then, STMs, AFMs, SECMs, and NSOMs have been used in many different ways to perform sophisticated lithography; several examples are described in a subsequent section.

Advantages of SPL methods include resolution that, for AFM and STM methods, approaches the atomic level, the ability to generate features with nearly arbitrary geometries, and the capability to pattern over surface topography that deviates significantly from planarity.⁸² These methods are serial techniques, however, and have writing speeds that are typically limited by the mechanical resonances of the tips and the piezoelectric elements that maintain constant separation between the tips and the sample. Research is underway to increase the speed of these methods by incorporating integrated arrays of tips that can write in parallel by using new designs for tips^{83,84} and by incorporating piezoelectric elements that have high resonance frequencies.^{82,85} Unless these approaches yield a huge increase in speed, it is likely that SPL methods will be better suited for formation of masters than for replication.

2.2. Replication against Masters by Methods Based on Physical Contact

The limitations to the use of projection photolithography with transmission optics to generate features with dimensions <100 nm (the so-called “100 nm-barrier”) *may* have opened the door to new technologies. Although photolithography has circumvented many limitations during its development and certainly cannot be neglected for nanofabrication, the limitations that it now faces are based on the physics of diffraction and of interactions of high-energy photons with matter and may be harder to overcome. As a result, it is now worth considering nonphotolithographic methods for pattern transfer. Some promising nonphotolithographic methods for nanofabrication include printing,⁸⁶ molding,⁸⁷ and embossing.⁸⁸ In fact, replica molding (or cast molding) with a UV (or thermally) curable precursor material and embossing (or imprinting) with a rigid master have already been widely used in industry to manufacture microstructures and some nanostructures: examples include diffraction gratings, holograms, and compact disks (CDs); these systems require replication of features with a fidelity ranging from ~200 nm to 10 μm.^{2,87,88} In these techniques, the resolution is mainly determined by van der Waals interactions, by wetting, by kinetic factors such as filling of the capillaries on the surface of a master, and by the properties of materials (for example, changes in dimensions with

changes in temperature or pressure, with wear, and on passing through phase transitions). They are not limited by optical diffraction. In research applications, replication techniques based on physical contact can now produce complex three-dimensional structures with features as small as a few nanometers, a resolution that would be extremely difficult to achieve using photolithography.^{47,89–91} Replica molding down to the molecular level (molecular imprinting) has also been reported, but we feel that the interpretation of these results is still ambiguous.^{92,93}

2.3. Pattern Formation Using Self-Assembly

One family of radically different approaches to fabrication of nanostructures is based on self-assembly.²³ The concept of self-assembly originates from biological processes such as the folding of polypeptide chains into functional proteins and chains of RNA into functional t-RNAs,⁹⁴ the formation of the DNA double helix,⁹⁵ and the formation of cell membranes from phospholipids.⁹⁶ In self-assembly, subunits (molecules or meso-scale objects) spontaneously organize and aggregate into stable, well-defined structures based on noncovalent interactions. The information that guides the assembly is coded in the characteristics (for example, topographies, shapes, surface functionalities, and electrical potentials) of the subunits, and the final structure is reached by equilibrating to the form of the lowest free energy. Because the final self-assembled structures are close to or at thermodynamic equilibrium, they tend to reject defects.^{23,40} Self-assembly is the route followed in biological systems for the formation of the cell and its components. These structures are enormously complex and very small, and their formation in biological systems suggests that self-assembly may provide a route to certain types of patterned nanostructures.

A variety of strategies for self-assembly have been demonstrated and employed to fabricate two- and three-dimensional structures with dimensions ranging from molecular, through mesoscopic, to macroscopic sizes.⁹⁷ Examples of these structures include self-assembled monolayers,^{45,98} structures (micelles, liposomes) derived from aggregated surfactant molecules,⁹⁹ phase-separated block copolymers,^{100,101} crystallized proteins¹⁰² or colloidal particles,¹⁰³ and aggregated meso-scale objects.¹⁰⁴ Self-assembly is now being examined extensively for patterning at scales $>1\text{ }\mu\text{m}$, and applications are moving to smaller dimensions. Demonstrations, including microcontact printing of self-assembled monolayers,¹⁰⁵ reactive ion etching with thin films of block copolymers as masks,¹⁰⁶ and synthesis of mesoporous materials with aggregates of surfactants as templates,^{107,108} illustrate the capability and feasibility of self-assembly as a strategy for fabricating nanostructures. The development of these methods into practical routes to useful patterned nanostructures still requires great ingenuity. In microcontact printing (μCP), for example, the formation of defects, the distortion of patterns, the dimensional stability of the stamps, and registration must be understood and controlled.

2.4. Pattern Formation Using Controlled Deposition

Features with nanometer sizes can also be generated using various methods of controlled deposition. In addition to deposition induced by focused laser beams^{109,110} and focused ion beams (FIB),¹¹¹ cleaved edge overgrowth (CEO)^{112,113} and shadowed evaporation¹¹⁴ represent two attractive methods that fall into this category.

Cleaved edge overgrowth is a technique based on molecular-beam epitaxy (MBE).^{112,113} It takes advantage of the high accuracy of MBE in controlling the thickness of deposited superlattices. After cleavage, the cross-section of a multilayer film prepared by MBE offers nanometer-wide templates for the growth of other materials or for the fabrication of simple patterns of quantum structures of semiconductors. This technique has molecular-scale resolution but is limited in the types of patterns that it can produce. Although it is most commonly used and has highest resolution with MBE films, the same basic approach is also certainly suitable for use with films grown using other techniques.

In shadowed evaporation,¹¹⁴ a stencil mask is fabricated directly on, but raised slightly above, the surface of the sample; this mask forms shadows when the sample is exposed to a flux of atoms or molecules. The shadows may be produced by depositing the material to be patterned at an angle or by fabricating the mask with an overhang. Removal of the mask after deposition leaves a pattern defined both by the mask and the method of deposition. The gray scale that occurs at the edges enables formation of features with smooth gradients in thickness;¹¹⁵ these types of features are difficult to fabricate using other methods. When MBE is used with carefully selected conditions, patterns can be formed that are not simple geometrical images of the shadows. In these cases, self-organization of deposited crystalline material yields features that can be sharper and smaller than those on the mask;¹¹⁶ 100-nm crystalline features with tip radii as small as 10 nm have been demonstrated.¹¹⁷ If the flux is incident on the sample at an angle, features in the pattern can be much smaller than those in the mask.^{114,118} Early work demonstrated a factor of 5 reduction in feature size with this technique.¹¹⁴ The method has been extended to glancing angle deposition on corrugated surfaces;^{119,120} features as small as 15 nm were generated in this way.^{120,121} Shadowed evaporation techniques occupy an important niche in the fabrication of certain types of nanostructures, but they are limited in the types of patterns that they can produce. They cannot form, for example, densely packed features with sizes significantly smaller than those in the masks.

2.5. Size Reduction

While it has been expensive or difficult to fabricate structures directly at the nanometer scale, a number of procedures have been developed that reduce the size of features that can be routinely produced by conventional microlithographic techniques. These

procedures demonstrate a cost-effective strategy for the fabrication of certain types of nanostructures that does not require access to high-resolution lithographic techniques. The most commonly used approaches for size reduction are based on physically isotropic deformation or shrinkage of amorphous materials^{122–127} and chemically anisotropic etching of single crystals.^{128,129}

In isotropic deformation (for example, drawing of glass fibers^{122–124} or compression of poly(dimethyl siloxane) (PDMS) molds^{125–127}), size reduction in one (or two) direction(s) is obtained at the expense of an increase in dimension in the other two (or one) dimensions. The mechanical deformation can be made reversible by using an elastomeric material.^{125–127} This reversibility yields an attractive capability—the feature size can be continuously reduced and iteratively adjusted by controlling the extent of deformation. The deficiency of methods based on mechanical deformations is that they depend on uniform distortion in the material; the level of uniformity necessary at the <100-nm scale may be difficult to achieve.

In anisotropic etching (for example, etching of Si-(100) in an aqueous KOH solution),^{128,129} the lateral dimension(s) between trenches decreases in a controlled way as the etching proceeds. By controlling the etching time, the feature size can be continuously reduced. This technique is probably most useful for generating simple patterns of nanostructures and in most cases must be combined with other techniques.

3. Current Technologies with Broad Flexibility in Patterning

The desire for features with sizes smaller than 100 nm in microelectronics and the interest in nanoscience motivates the development of photolithographic methods based on nanometer-wavelength electromagnetic radiation and lithographic techniques that use particles with de Broglie wavelengths in the range of angstroms.^{42,130} Table 2 compares current UV photolithography with advanced lithographic technologies (short-wavelength photolithography and beam-writing methods). All of these techniques have broad flexibility in patterning and are capable of generating structures with lateral dimensions in the range of a few nanometers to a few hundred micrometers.^{42,49,130} This section discusses some aspects of these methods with emphasis on photolithography and e-beam writing.

Table 2. Current Technologies with Broad Flexibility in Patterning^a

using	writing	replication	refs
photons			
UV	no	yes	48, 49, 131
DUV	no	yes	27, 49, 131
EUV	no	yes	55, 56
X-ray	no	yes	55, 56, 131
particles			
focused electrons	yes	no	42, 49, 69, 136
focused ions	yes	no	49, 111, 142

^a In this table, yes means this technique is practical for writing or replication of features of ≤100 nm; no means this technique cannot practically be so used.

Photolithography. As discussed in a previous section, photolithography is usually carried out using one of two different schemes: contact (or proximity) printing or projection printing.⁴⁸ In contact printing, the photomask is in physical contact with, or in close proximity to, the resist film. The minimum feature size that can be obtained by this process is primarily determined by diffraction that occurs as light passes through the gap between the mask and the resist. Even with the use of elaborate vacuum systems to pull the mask and substrate together, it is still difficult in practice to reduce the gap between a conventional rigid mask and a rigid, flat substrate to less than ~1 μm over large areas. As a result, the resolution of contact mode photolithography is typically 0.5–0.8 μm when UV light (360–460 nm) is used. Contact-mode photolithography is not seriously considered as a generally useful technique because the required mechanical contact can damage fragile structures on the mask or the sample, the features on the mask must be as small as those generated in the resist, and slight unwanted lateral motion of the mask when it is pulled against the mask makes accurate alignment to existing features difficult.

In projection printing, a system of lenses placed between the mask and the resist film projects a high-quality, demagnified (usually by a factor of 4) image of the mask onto the resist. With this approach, the features on the resist can be significantly smaller than those on the mask, contact with the sample is not required, and alignment or registration can be relatively straightforward. Essentially all integrated circuits are manufactured by projection photolithography, using equipment known as a step-and-repeat machine (or stepper).³⁸ The theoretical resolution (R) of an optical system for projection printing is limited by Rayleigh diffraction (eq 1)¹³¹ where λ is the wavelength of the illuminating light, NA is the numerical aperture of the lens system, and k_1 is a constant that depends on the imaging technology and process control but typically must be >0.7 for adequate production yield. This equation indicates that

$$R = k_1 \lambda / \text{NA} \quad (1)$$

improvements in optical resolution can be achieved either by increasing the numerical aperture or by reducing the wavelength of the illuminating light. For the purposes of this review, we assume that the numerical aperture cannot be increased beyond ~1, a value that, at least for small areas, can be approached now. Reducing λ , then, has historically represented a promising route to achieving significant decreases in R . This inference is consistent with experience in the microelectronics industry: production of 250-nm structures is achieved with wavelengths of 248 nm (KrF excimer laser), and sub-150-nm features (due in the year 2001) are generally, but not universally, thought to require 193-nm radiation (ArF excimer laser).⁴¹

In addition to the resolution, the spatial depth over which the image of the mask is faithfully produced (the depth of focus, DOF) is an important quantity; increasing this value to acceptable levels poses a technical challenge for projection photolithography.

The DOF is related to the wavelength and the numerical aperture by eq 2

$$\text{DOF} = 0.5k_2\lambda/\text{NA}^2 \quad (2)$$

where k_2 is a constant that depends on the aberrations of the imaging system and tends to be in the range of 1–2. In practical terms, there is significant blurring and distortion of the image for distances beyond the DOF from the image plane. At a minimum, the image must not degrade over distances $\pm 0.5 \mu\text{m}$ from the image plane (i.e., $\text{DOF} = 1 \mu\text{m}$) in order to have the projected image stay in focus throughout the thickness of films of photoresists that are typically used. In practice, it is useful to have a DOF larger than $1 \mu\text{m}$ in order to have some insensitivity to slight variations in the thickness of the resist or the position of the surface of the substrate.

To lower the NA or to increase the DOF, it is necessary to decrease λ to maintain the resolution. Since changing λ is usually not easy, schemes that increase the DOF and R through a reduction in k_1 and/or an increase in k_2 are attractive. Strategies for achieving this result include the use of phase-shifting masks,¹³² off-axis illumination,¹³³ optical proximity correction,¹³⁴ and chemically amplified photoresists.^{51,58} Many of these methods are extremely useful, and clever implementation of combinations of these techniques or development of new ones may allow for continued increases in resolution without changes in wavelength. One process uses advanced phase-shifting masks and optical proximity correction with 248-nm light to fabricate features as small as 100 nm.¹³⁵ It is somewhat clearer that, in principle, large increases in resolution can be achieved with similarly large decreases in the wavelengths of the illuminating sources. Unfortunately, few materials are suitable for lenses that are transparent at wavelengths below $\sim 200 \text{ nm}$. Even though fused silica will likely be used for 193 nm lithography, this material becomes increasingly absorbing below 200 nm. While there are now substantial efforts to develop grades of silica that are more transparent and less susceptible to photodamage than those currently available, new materials such as CaF_2 or a switch to reflective optics may be required for future generations of photolithographic systems.

X-ray Lithography. X-ray lithography (XRL) represents the short-wavelength limit of what is currently being explored for photon-based approaches to lithography.^{55,56,130} Two types of schemes have been demonstrated for XRL: soft X-ray (or EUV) projection lithography that uses reflective optics^{55,56} and proximity XRL with wavelengths near 1 nm.¹³⁰ Although routine fabrication of structures as small as $\sim 30 \text{ nm}$ has been demonstrated by proximity XRL, the implementation of this technique for IC production is slowed by the lack of a commercially feasible way to produce the required masks and by the absence of suitable optics to project or reduce the image of the mask. In addition, reproducibly placing the mask in close proximity to ($\sim 10 \text{ mm}$) but out of physical contact with the substrate can be challenging.

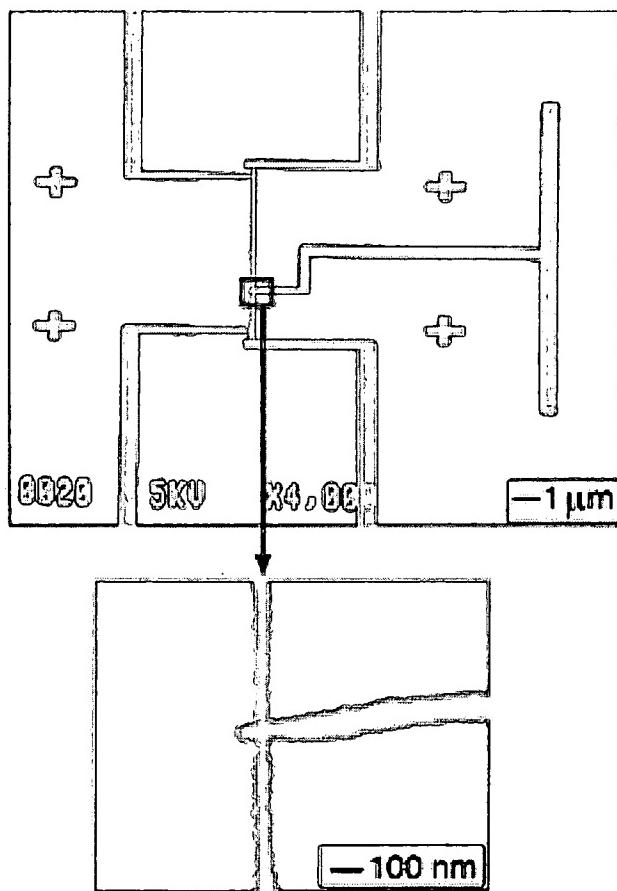
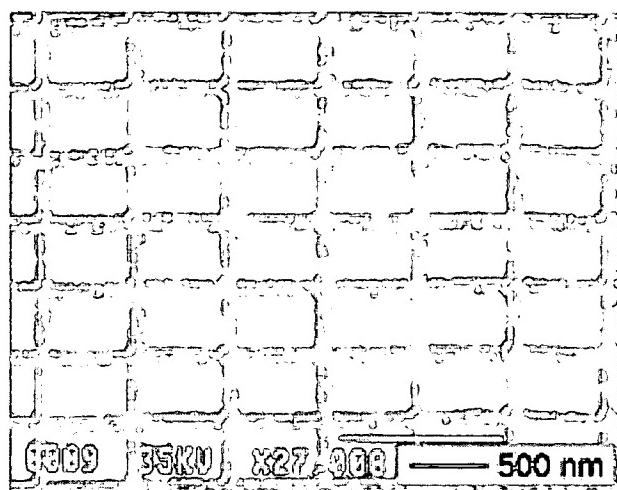


Figure 1. SEM images of nanostructures of gold that were fabricated using e-beam writing in thin films of PMMA resist, followed by evaporation of gold and lift-off (courtesy of Prof. Lydia Sohn of Princeton University).

Electron-Beam Lithography. Focused electron beams, beyond observing samples as in scanning electron microscopy (SEM) or transmission electron microscopy (TEM), can also be used to form patterned nanostructures in an electron-sensitive resist film.^{69,136} In typical e-beam lithography, a tightly focused beam of electrons scans across the surface of a layer of resist, such as poly(methyl methacrylate) (PMMA).¹³⁷ Interaction of the electron beam with the resist causes local changes in its solubility, and in the case of PMMA, the electrons induce local chain scission

Table 3. New Technologies with Broad Flexibility in Patterning^a

pattern formation using	writing	replication	refs
physical contact			
nanomachining (STM, AFM, NSOM, and electrochemical methods)	yes	no	144–159
soft lithography (μ CP, MIMIC, μ TM, REM, and SAMIM)	no	yes	38, 161
embossing/imprinting	no	yes	88, 91, 194
photons			
near-field phase-shifting photolithography	no ^b	yes	39, 201, 203
topographically directed photolithography	no ^b	yes	204
deposition			
topographically directed etching	no ^b	yes	205
particles			
metastable atom lithography	no	yes	209, 210
size reduction			
glass drawing	yes	no	122–124
compression of elastomeric mold	yes	yes	125–127
shadowed evaporation	yes	no	114–116
controlled reactive spreading	yes	no	191

^a In this table, yes means this technique is practical for writing or replication of features of ≤ 100 nm; no means this technique cannot practically be so used. ^b With possible specialized exceptions.

and formation of micropores that causes the material to be soluble in a developer that consists of methyl-isobutyl ketone and 2-propanol.⁴⁸ The short wavelength associated with high-energy electron beams (for example, ~ 0.005 nm for 50 keV electrons) gives e-beam writing an extremely high resolution capability; 0.5-nm focused spots were possible very early in the development of this technique,¹³⁸ and high-brightness spots with diameters as small as 0.25 nm are now possible.^{139,140} For e-beam lithography, the resolution is mainly determined by the scattering of primary and secondary electrons in the resist film and the substrate. Patterns with features as small as ~ 50 nm can be routinely generated by e-beam writing.¹⁴¹ By using thin (10–100 nm) membranes as substrates to minimize the scattering problem, structures as fine as ~ 2 nm have been obtained.⁴² Figure 1 shows SEM images of nanostructures of gold fabricated using e-beam writing in PMMA film, followed by evaporation of gold and lift-off.

Conventional direct-write e-beam technology is a sequential process that exposes a film of resist in a serial fashion; it is impractical for mass production because of the lengthy writing time (approximately 1 h) per wafer (4 in.).⁶⁹ Electron beam writers, therefore, tend to be used mostly to produce photomasks in optical lithography or to produce small numbers of nanostructures for research purposes. It is also widely used in certain niche applications where optical lithography simply fails: fabrication of high-frequency GaAs field-effect transistor (FET) devices that requires resolution down to ~ 100 nm and manufacturing of relatively low-volume products such as application-specific integrated circuits (ASIC).⁴⁹ Electron-beam projection techniques, such as SCALPEL (scattering with angular limitation projection electron lithography), that have the resolution approaching direct-write systems and the parallelism of projection lithographic systems are very promising and are now being intensely developed for mass production of patterned nanostructures.⁶⁹

Focused Ion Beam Lithography. Focused ion beam (FIB) lithography is another attractive tool for writing nanostructures.^{49,111} Features as small as ~ 6 nm have been fabricated using a 50 kV Ga⁺ two-lens

system.¹⁴² FIB lithography is also a serial technique, but it has at least two advantages over electron-beam lithography: (i) FIB has a higher (approximately 2 orders of magnitude) resist exposure sensitivity than focused electron beam and (ii) FIB has negligible ion scattering in the resist and very low backscattering from the substrate. The damage to samples induced by high-energy ions is a major problem for FIB. Nevertheless, FIB is likely to remain useful for generation of patterned nanostructures in resist films, patterned implantation, repair of defects in photo- and X-ray masks, inspection in IC processes, failure analysis, and surface characterization (for example, in secondary ion mass spectroscopy, SIMS).^{111,143}

4. New Methods with the Potential for Broad Flexibility in Patterning

The enormous expense of the advanced lithographic techniques discussed in section 3 is perhaps one of their most significant disadvantages.⁴² Thus, the development of cost-effective methods that are capable of writing or replicating nanostructures in a wide range of materials represents one of the greatest technical challenges now facing nanofabrication. The precise meaning of "cost-effective" depends on the application. For successful, high-throughput fabrication facilities such as those used in manufacturing microprocessors and memories, it may be possible to recover high operating costs but the projected capital costs (\$1–10 billion per facility) are daunting; for consumer markets with short product lifetimes and low margin, both capital and operating costs must be controlled. A range of techniques for nanofabrication that may have economics superior to those now used have been recently demonstrated, and those with broad flexibility in patterning are summarized in Table 3 and described in detail below.

4.1. Nanomachining with Scanning Probes

The demonstrated ability of the scanning probe microscope (for example, STM, AFM, NSOM, and SECM) to image and modify surfaces with atomic resolution suggests opportunities for their use in

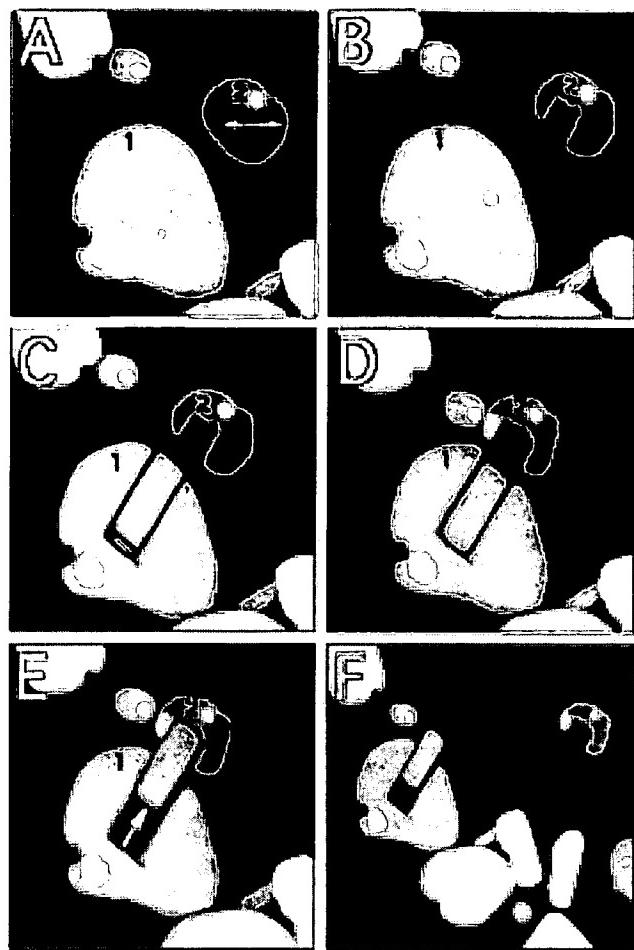


Figure 2. AFM images of selected steps in the fabrication of a nanostructure (containing three interlocking pieces) by AFM lithography and manipulation (courtesy of Prof. Charles Lieber of Harvard University).^{146,159} (A) Initial positions of two MoO_3 nanocrystals, crystal 1 and crystal 2 (the preferred sliding directions are indicating by two-headed arrows). (B) A 52-nm notch was defined in crystal 2 by nanomachining. (C) A 58-nm free rectangle (latch) was machined in crystal 1, and crystal 2 was translated toward crystal 1. (D) Crystal 2 was translated to align the notch with the latch. (E) The latch was moved into the notch of crystal 2. (F) The latch was broken after a force of 41 nN was applied to the latch axis. Reprinted with permission from *Science* 1996, 272, 1158. Copyright 1996, American Association for the Advancement of Science.

generating nanostructures and nanodevices.^{79,144} Atomic force microscopy has been the most widely used technique; typical approaches include the use of an AFM tip to scratch nanostructure in soft materials,^{145,146} to expose thin films of resist,^{147,148} to induce and/or enhance oxidation of H-terminated Si(100),¹⁴⁹ to change the headgroups or packing density of organic monolayers catalytically,¹⁵⁰ and to "write" 30-nm patterns of alkanethiols on gold.¹⁵¹ STM tips have been used to alter the structure or order of organic monolayers,¹⁵² to oxidize hydrogen-terminated silicon,^{78,153} to induce phase transition in a solid material,¹⁵⁴ and to manipulate atoms or molecules.^{155,156} Other uses of scanning probes include an NSOM tip to expose photoresist films^{15,157,158} and an SECM tip to deposit metals.⁸⁰ Figure 2 shows AFM images of a nanostructure that has been machined in a thin film of MoO_3 .^{146,159} The AFM tip

was also used to manipulate and transfer this carved nanostructure.

The smallest features that have been fabricated using SPM lithography are only a few tenths of a nanometer in dimension.¹⁵⁵ The system based on H-terminated Si(100) is most important for applications in microelectronics since almost all silicon devices are fabricated from this type of wafer. Quate et al. have used this approach to fabricate the first working device with an AFM—a functional MOSFET.¹⁶⁰ More recently, SPM lithography in H-Si(100) has been used by a number of groups to fabricate quantum devices such as single-electron transistors (SETs) and metal-oxide junctions.^{79,149}

Despite enormous advances in this area, the use of SPM lithography in IC manufacturing remains to be developed seriously. Like e-beam writing, SPM lithography is a serial process and its slow speed will likely limit its use only to master writing. Unlike lithography with electrons, there is no equivalent to projection printing with SPMs. The only obvious route to increase the speed of SPM methods is to build arrays of probes to make this technique semi-parallel.^{82,83} MacDonald et al. have fabricated structures that contain thousands of STM tips.⁸⁴ Although these approaches may increase the throughput of SPM lithography, they will also increase significantly its complexity and cost.

4.2. Soft Lithography

Soft lithography (Figure 3) is the collective name for a set of lithographic techniques—replica molding (REM), microcontact printing (μ CP), micromolding in capillaries (MIMIC), microtransfer molding (μ TM), solvent-assisted micromolding (SAMIM), and near-field conformal photolithography using an elastomeric phase-shifting mask—that has been developed as an alternative to photolithography and a replication technology for micro- and nanofabrication.^{38,39,161} These techniques use a patterned elastomer (usually PDMS) as the mold, stamp, or mask to generate or transfer the pattern. Soft lithography offers immediate advantages over photolithography and other conventional microfabrication techniques for applications in which patterning of nonplanar substrates, unusual materials, or large area patterning are the major concerns. It is especially promising for microfabrication of relatively simple, single-layer structures for uses in cell culture, as sensors, as microanalytical systems, in MEMS, and in applied optics. The initial success of soft lithography indicates that it has the potential to become an important addition to the field of micro- and nanofabrication. Because two recent review articles have been devoted to soft lithography,^{38,161} this section will concentrate on soft lithographic techniques that have been demonstrated at the ≤ 100 -nm scale.

Replica Molding (REM). The capability and feasibility of replica molding can be greatly enhanced by incorporating elastomeric materials into the procedure, albeit at some cost in reproducibility (Figure 3A).^{127,163} In REM, an elastomer (for example, PDMS) is cast against a rigid master and the elastomeric replica is subsequently used as a mold against which

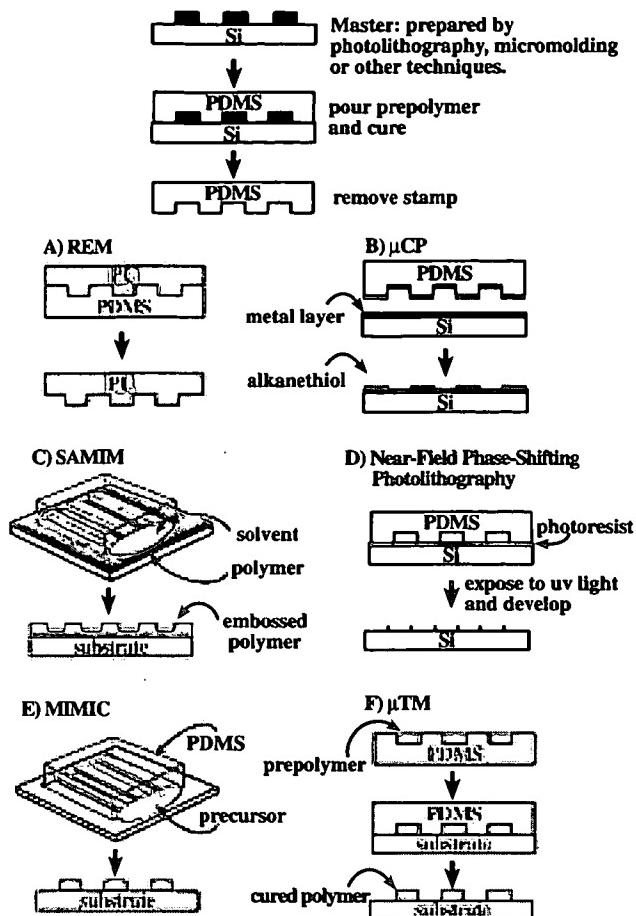


Figure 3. Schematic procedures describing soft lithographic methods^{38,161} and near-field phase-shifting photolithography.^{38,162}

new replicas are produced in organic polymers. The introduction of elastomers into replica molding makes it easier to preserve small, fragile structures on the original master; the low surface energy (~ 21.6 dyn/cm) of PDMS, in particular, also allows the replica

to be separated from the mold easily.¹⁶⁴ An elastomeric mold also offers the opportunity to manipulate the size and shape of structures on the mold by mechanical or thermal deformation. For example, we have been able to reduce the lateral dimension of nanostructures from ~ 50 to ~ 30 nm by replica molding against a PDMS mold which is compressed mechanically.⁴⁷

Figure 4 illustrates the use of REM to generate patterned nanostructures. Figure 4A shows an AFM image of chromium nanostructures on a master that was fabricated using light guiding to pattern the deposition of chromium atoms.¹⁶⁵ Figure 4B shows an AFM image of a polyurethane (PU) replica that was prepared from a PDMS mold cast from this chromium master.⁴⁷ Although this process used replica molding twice, the vertical dimension of the chromium nanostructures was reproduced with an accuracy of better than 5 nm over a substantial area (~ 1 mm 2). Figure 4C shows an AFM image of gold nanostructures on another master (fabricated by Lydia Sohn at Princeton University using a combination of e-beam writing in PMMA, gold evaporation, and lift-off). Figure 4D shows an AFM image of nanostructures in polyurethane generated by replica molding against a PDMS mold cast from this second master. Using this procedure, we have successively produced more than 20 copies of PU nanostructures from a single master; these polymer nanostructures are indistinguishable from each other.

This work based on replica molding against an elastomeric mold has demonstrated a practical protocol for nanomanufacturing; that is, production of multiple copies of indistinguishable nanostructures from a single master, rapidly and economically.⁴⁷ The challenge for the future in considering this technique for use in microelectronics or optics is to transfer the structural information present in the polymer into electrical or optical materials, to control distortions in the dimensions of the master and the replicas on

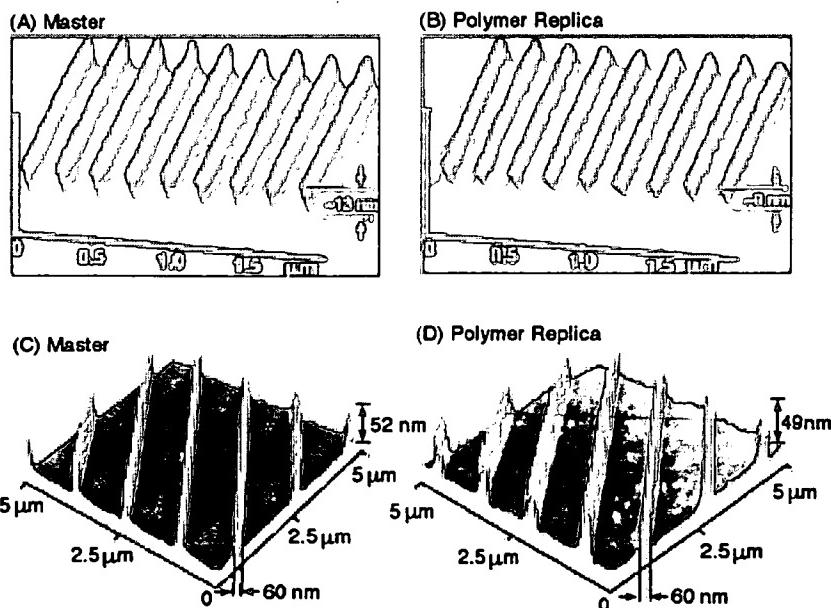


Figure 4. (A,B) AFM images of chromium nanostructures on a master, and a polyurethane replica prepared from a PDMS mold cast from this master. (C,D) AFM images of gold nanostructures on another master, and a polyurethane replica produced from different a PDMS mold cast from this master.⁴⁷

casting and curing the polymers and during use, and to develop schemes that allow the registration required for multilevel fabrication.

Microcontact Printing (μ CP). Microcontact printing was mainly developed with self-assembled monolayers (SAMs) of alkanethiolates on gold and silver.^{105,166} The procedure for carrying out μ CP in these systems is remarkably simple (Figure 3B): an elastomeric PDMS stamp, inked with an appropriate solution of alkanethiol, is brought into contact with the surface of a substrate to transfer the ink molecules to those regions of the substrate that contact the stamp. The success of μ CP relies on the conformal contact between the stamp and the surface of the substrate, on the rapid (less than 1 sec!) formation of highly ordered monolayers as a result of self-assembly,¹⁶⁷ and on the autophobicity of the SAM, which effectively blocks the reactive spreading of the ink across the surface.¹⁶⁸ Microcontact printing is an additive process that minimizes waste of starting materials. It is intrinsically parallel: patterned SAMs can be formed over relatively large areas ($\sim 50\text{ cm}^2$) in a single impression.¹⁶⁹ It is also applicable to curved substrates and, hence, is useful in some kinds of 3-D fabrication,^{170–172} although the formation of patterned SAMs is at present, intrinsically a 2-D process. It can also be used on inner surfaces that are not accessible to any plausible projection lithographic scheme.¹⁶⁹

Microcontact printing has been used with a number of systems including SAMs of alkanethiolates on gold,¹⁷³ silver,¹⁶⁶ and copper;^{174,175} SAMs of alkylsiloxanes on HO-terminated surfaces;^{176–183} and SAMs of RPO_3H_2 on aluminum.¹⁸⁴ Of these, alkanethiolates on gold and silver presently give the highest resolution patterning; most other systems have been demonstrated only at scales $> 1\text{ }\mu\text{m}$. Microcontact printing can routinely form patterns of alkanethiolate SAMs on gold and silver with in-plane dimensions at the scale of $\sim 500\text{ nm}$ and with some difficulty with dimensions $< 100\text{ nm}$.¹⁸⁵

The patterned SAMs can be used either as resists in selective wet etching¹⁸⁶ or as templates in selective deposition^{177–179,181,183} to form patterned structures of a variety of materials: metals, silicon, liquids (by dipping or condensation from the vapor), organic polymers (by dipping or polymerization of monomer), and even biological species.¹⁸⁷ Figure 5 shows SEM images of nanostructures of gold and silver that were fabricated using μ CP, followed by selective wet etching. Lateral force microscopy (LFM) shows that patterned SAMs of hexadecanethiolate on gold have an edge roughness that is less than $\sim 50\text{ nm}$.¹⁸⁸ These results indicate that μ CP has the capability to produce structures with lateral dimensions $< 100\text{ nm}$. We believe that the edge resolution of nanostructures in coinage metals fabricated by a combination of μ CP and wet etching is largely determined by the grain size of the metal films, the etching process, or a combination of these factors. The smallest features fabricated with a combination of μ CP of SAMs and wet etching are trenches in gold that are $\sim 35\text{-nm}$ wide and separated by $\sim 350\text{ nm}$ (Figure 5B).¹⁸⁵ The minimum feature size that can be achieved by μ CP

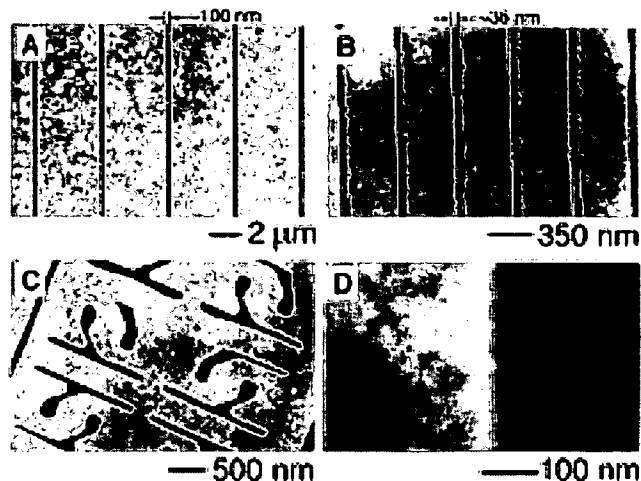


Figure 5. SEM images of nanostructures of gold (A,B) and silver (C,D) fabricated using μ CP with hexadecanethiol, followed by selective wet etching. (A) An array of $\sim 100\text{-nm}$ trenches fabricated in gold by μ CP with controlled reactive spreading of hexadecanethiol under water.¹⁹¹ (B) Array of $\sim 35\text{-nm}$ trenches fabricated in gold by μ CP with hexadecanethiol (courtesy of Dr. Hans Biebuyck of IBM).¹⁸⁵ (C,D) Patterned structures in silver with feature sizes of $\sim 200\text{ nm}$ fabricated by μ CP with hexadecanethiol.¹⁶⁶

has still not been completely defined, and continuing systematic study on the mechanical properties of the stamp and of interactions between the stamp, the ink, and the substrate will be useful for the optimization of μ CP for use in the $< 100\text{-nm}$ regime.^{98,189}

Solvent-Assisted Micromolding. Solvent-assisted micromolding (SAMIM) shares operational principles with embossing, except that SAMIM uses a solvent instead of temperature to "soften" the polymeric material and an elastomeric PDMS mold rather than a rigid one to emboss relief structures into the surface of a substrate.¹⁹⁰ In SAMIM (Figure 3C), a PDMS mold is wetted with a good solvent for the polymer to be embossed and brought into contact with the surface of that polymer. The solvent is selected to dissolve (or "soften") the substrate without affecting the PDMS mold. After the solvent dissipates and/or evaporates, the mold is removed and a patterned relief structure complementary to that on the surface of the mold remains. This structure forms by molding the thin layer of fluid (probably, gellike) material generated by interaction of the polymer and the solvent.

SAMIM has been used with a wide variety of organic polymers: polystyrene, PMMA, Novacal photoresists, poly(vinyl chloride), cellulose acetate, and precursors to conjugated organic polymers.^{190,192} Its only requirement is for a relatively volatile solvent that dissolves the substrate and wets (but does not significantly swell) the surface of the PDMS mold. Other materials can also be added into the solvent; these materials are then incorporated into the resulting relief structures. SAMIM is capable of replicating complex quasi 3-D relief structures over relatively large areas in a single step. Figure 6 shows AFM images of nanostructures that we have generated using SAMIM: parallel lines $\sim 60\text{-nm}$ wide and $\sim 50\text{-nm}$ high formed in a thin film of photoresist. These features rest on top of a thin underlying film of the

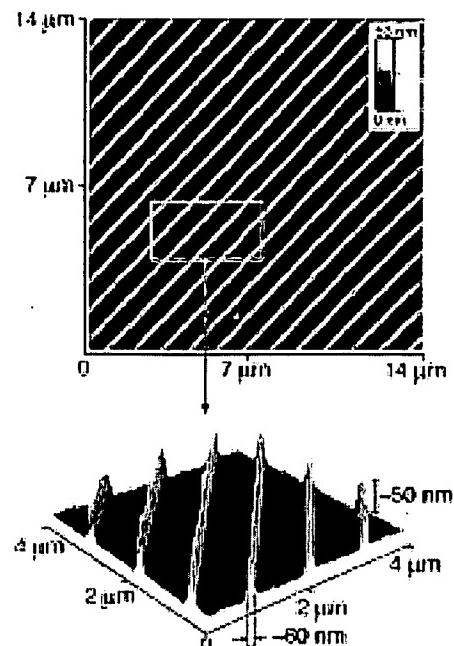


Figure 6. AFM images of polymeric nanostructures fabricated using SAMIM in a thin (~0.4 mm thick) film of Microposit 1805 spin-coated on Si/SiO₂.¹⁹⁰ Reprinted by permission from *Adv. Mater.* 1997, 9 (8), 651–654. Copyright 1997, Wiley-VCH Verlag GmbH.

polymer; similar underlying films are also often formed in replica molding and in embossing. If necessary, this thin film can be removed by reactive ion etching (RIE) in an O₂ plasma without excessive damage to the surface topography that represents the pattern.

An important characteristic of SAMIM is that it is “self-cleaning”. Dust particles on the surface of the stamp tend to remain in the molded polymer. Each cycle of use therefore cleans the mold and limits the influence of adventitious particulates to one cycle of replication. The extent to which the surface of the mold is eventually wetted by and damaged by the polymer being molded remains to be established.

4.3. Embossing with Rigid Masters

Conventional embossing uses a rigid master (for example, a master made of nickel or SiO₂) to imprint relief structures into a thermoplastic polymer (for example, polycarbonate or PMMA) that has been thermally softened.^{2,88} It is a simple, reliable, cost-effective, and high-throughput process and is the standard for manufacturing replicas of holograms, diffraction gratings, and compact disks (CDs).^{2,88} Recently, this technique has been reexamined as a method for producing nanometer-sized structures of semiconductors, metals, and other materials commonly used in microelectronic circuitry or information storage.^{91,193} Chou et al. have used embossing with a Si/SiO₂ master to generate features in silicon with lateral dimensions as small as ~25 nm.⁹¹ It is remarkable that such nanostructures can be generated over areas as large as 3 cm²,¹⁹⁴ given the fact that it is nontrivial to bring two rigid substrates into conformal contact (for example, one cannot reproducibly achieve zero gaps in contact-mode photoli-

thography) and then separate them while a thin film of polymer remains between them. Using this technique, Chou et al. have fabricated prototype functional devices such as silicon field-effect transistors (FETs).¹⁹⁵ More recently, they and other groups have explored this technique as a potential method for producing binary structures for high-density information storage, including arrays of nanometer-sized bars of cobalt or nickel for quantized magnetic disks and nanometer-sized pits in polymer films for optical disks.¹⁹⁶ The initial success of this technique indicates that it may be worthwhile to reexamine other existing microlithographic techniques for their potential in nanofabrication.

Embossing shares with SAMIM the characteristic that it is self-cleaning. Release of the polymer being embossed from the master, damage to the master while it is under pressure, and the importance of distortions in the embossed structures due to thermal cycling during molding all remain to be defined.

4.4. Near-Field Phase-Shifting Photolithography

The resolution in projection photolithography is fundamentally limited by the wavelength of the light used for exposure and by the numerical aperture of the imaging optics.⁴⁸ Contact-mode photolithography with an amplitude mask, on the other hand, has a resolution that can be made exceedingly high without changing the wavelength by simply reducing the size of the gap between the mask and by minimizing the thickness of the resist. Projection and contact techniques have different dependence on wavelength in part because the former does not allow the photoresist to interact with evanescent waves, which are nonpropagating electromagnetic modes that can modulate the intensity at spatial frequencies higher than the diffraction limit allows. These waves are confined to a narrow region near the mask and cannot propagate through imaging optics in projection systems. Approximate calculations of the near field show that for a slit with a width of $\lambda/2$, the intensity in the evanescent modes (which, for this situation, is slightly less than the intensity in the propagating modes at zero separation from the mask) decays by a factor of ~10 over a distance of $\sim\lambda/4$ from the mask, where λ is the wavelength of the light evaluated in the medium into which it propagates as it passes through the mask.¹⁹⁷

On the basis of NSOM imaging results, better than $\lambda/10$ should be achievable with contact photolithography and even smaller features should be possible if highly nonlinear resists are used.¹⁵ Even elaborate vacuum systems, however, cannot pull a rigid or semiflexible mask close enough (even separations less than ~1 μm can be difficult to achieve) to the resist over large areas to take advantage of the full potential of near-field optics, because dust on the resist or the mask, nonuniformities in the thickness of the resist, or bowing of the mask or the substrate that supports the resist prevent the necessary positioning. NSOM photolithography avoids this problem through the use of narrow, subwavelength sources of light that can be scanned within ~10 nm of the surface of the resist.¹⁵ Unfortunately, this technique, like other

scanning probe methods, has the drawback that patterning must occur in a serial fashion.

There have been several attempts to design specialized masks for eliminating the mask-resist gap in large area contact-mode photolithography.^{198,199} Until recently, such masks have all been based on thin layers of rigid materials that can be bent and pulled close to the sample by applying external forces. These methods yielded encouraging initial results: the smallest features generated in the first experiments were ~ 400 nm, and since then, features as small as ~ 100 nm have been achieved.²⁰⁰ In all of these methods, however, patterning over large areas was difficult and external forces were required to bring the mask and the resist into contact. As a result, many of the disadvantages of conventional contact photolithography—potential damage to mask and sample (resulting from contact, shear, and adhesion) and susceptibility to dust and other contaminants—remain.

A different approach to conformal near-field photolithography uses masks constructed from “soft” organic elastomeric polymers.^{39,128,162} These soft masks spontaneously and nondestructively come into conformal, atomic-level contact with layers of photoresist over areas that can exceed several hundred square centimeters without the need for external force. They completely eliminate the gap between projecting regions of the mask and the resist; atomic-level contact allows for exposure of the resist directly in the near field of the mask. Dust or other nonuniformities only locally frustrate contact. The masks are essentially insensitive to modest degrees of bowing or warping of the substrate and can even be applied to curved surfaces.

We have used elastomeric binary phase-shifting masks with conventional photoresists and polychromatic, incoherent light from low-cost ultraviolet lamps to produce ~ 90 -nm features over large areas on flat surfaces and on the surfaces of cylindrical lenses.^{39,162} By optimizing the construction of the masks, we generated lines as narrow as 50 nm.^{60,61} Figure 7 shows representative results. This resolution corresponds approximately to $\lambda_r/5$, where λ_r is the wavelength of the light used for exposure evaluated in the photoresist; it significantly exceeds the diffraction limit in air. Since the exposure of the top surface of the resist happens directly in the near field of the mask, we believe that features even smaller than 50 nm will be possible. It is likely that the resolution can be improved by reducing the wavelength of the light, the thickness of the resist, the thickness of the modulating component (in our initial work, the surface relief) of the masks, by increasing the index of refraction of the resist, by using surface-sensitive resists, or by a combination of these approaches.

With simple binary phase masks, it is possible to generate a wide variety of patterns that consist of lines with fixed width; producing lines with variable widths or other types of features was difficult. Schmid et al. have since described the addition of amplitude modulating components derived from thin layers of gold to elastomeric phase masks²⁰¹ or using feature

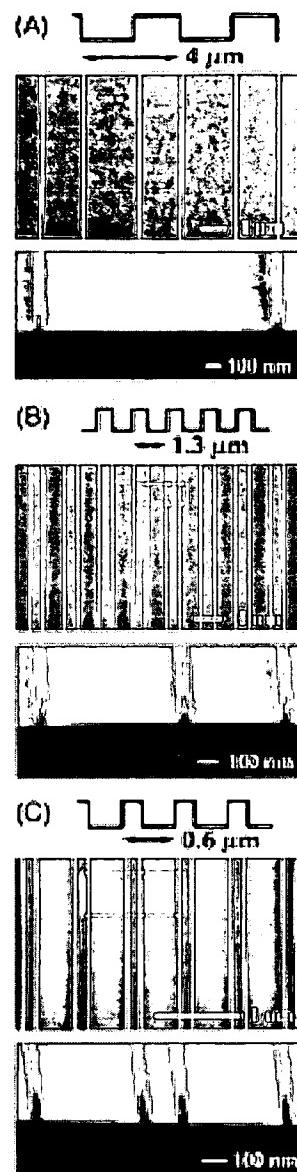


Figure 7. SEM images of lines in positive photoresist formed by near-field phase-shifting photolithography using a PDMS mask with 500-nm deep relief. The periodicity of the mask relief decreases from A to C.^{39,60,61,162}

sizes on the mask that are equal to or smaller than the wavelength of the light used for exposure.²⁰² This construction yields masks that have more flexibility in patterning than those based purely on phase modulation: in particular, lines and other more complex features with a wide range of sizes are possible.

We believe that there are two primary limitations inherent to methods based on near-field photolithography with an elastomeric mask: distortions that can arise from lateral deformation of the elastomer when it comes into conformal contact with the resist and vertical deformations that can cause sagging of the recessed regions of the masks.²⁰³ With the masks that are used now, lateral distortions are on the order of, or less than, 1 μm over areas of $\sim 1 \text{ cm}^2$. Stiffer elastomers and perhaps active control of the deformations of the masks may enable reductions in these distortions. Stiff elastomeric materials and thin elastomeric amplitude masks will also minimize or

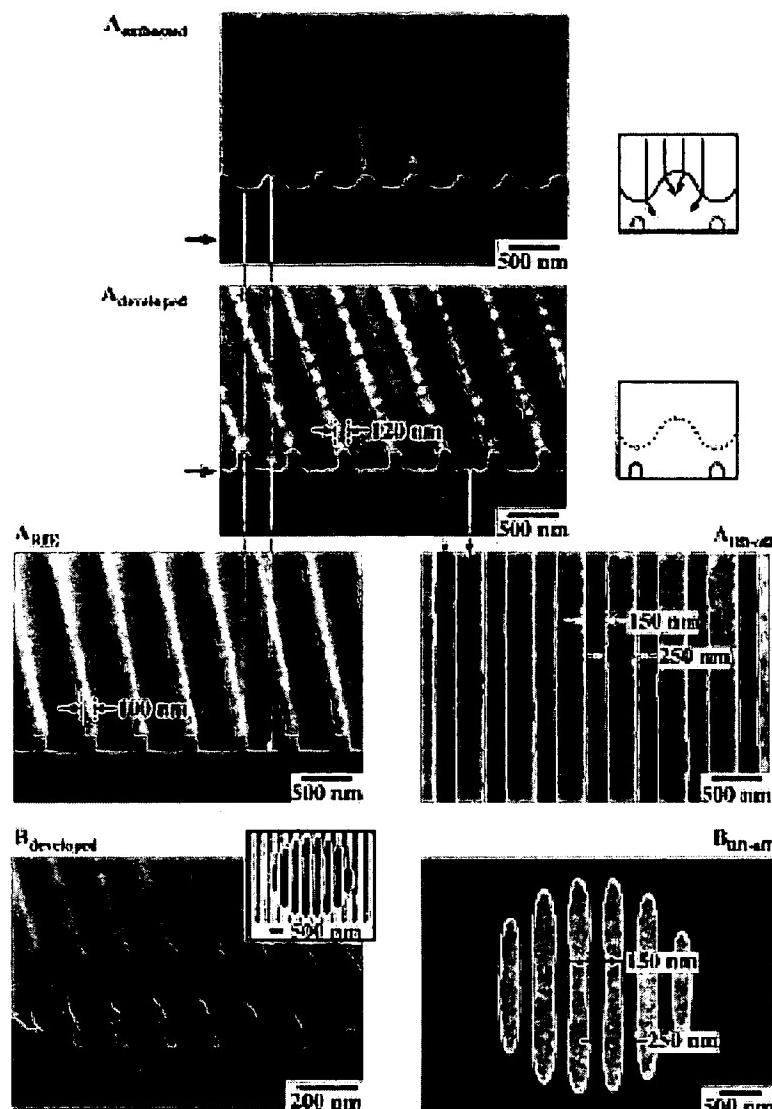


Figure 8. SEM images of nanostructures generated by topographically directed photolithography ($\lambda = 350\text{--}440\text{ nm}$).²⁰⁴ Dashed arrows show where the features originate. (A_{embossed}) Grating embossed on a 0.48- μm photoresist film with a 2400 lines/mm holographic grating; (A_{developed}) exposed for 2.75 s and developed for 1 min. The drawings suggest the exposure process schematically. The photoresist pattern was then transferred into silicon (A_{RIE}) by RIE and gold (A_{lift-off}) by lift-off. (B_{developed}) Embossed 2400 lines/mm holographic grating was covered with an amplitude mask of 3- μm circles separated by 11 μm and exposed for 1.85 s. (B_{lift-off}) The resulting pattern was transferred into gold by lift-off. Reprinted with permission from *Appl. Phys. Lett.* 1998, 73, 2893–2895. Copyright 1998, American Institute of Physics.

eliminate adverse effects of sagging. Even without further improvement, we believe that these techniques will be valuable for a range of applications that require rapid, low-cost nanopatterning over large areas. They currently provide one of the easiest experimental routes to nanostructures that can have a wide range of possible geometries.

4.5. Topographically Directed Photolithography

The patterned structure of photoresist generated by SAMIM has been used in a photolithographic technique we call topographically directed photolithography (TOP).²⁰⁴ In this method, a topographically patterned layer of photoresist (for example, an array of lenses or rectangular gratings) directs UV light inside the resist layer in the optical near field, during exposure. Development gives complex features with feature sizes from ~ 50 to ~ 200 nm over large areas. It uses no mask in the conventional sense, and

although it is a photolithographic technique, it circumvents many of the limitations of both conventional far-field lithography and near-field photolithography. Figure 8 shows SEM images of nanofeatures generated by this procedure. Subsequent process such as RIE or lift-off can transfer the pattern into other materials.

4.6. Topographically Directed Etching

This technique uses a topographically patterned surface to generate a pattern corresponding to the edges of the original pattern. It is, therefore, a technique similar to pure phase-shifting photolithography in the types of patterns it can generate: the edges of the original pattern become the pattern after the transfer step.²⁰⁵ In this technique (Figure 9), a layer of metal (gold or silver in the first demonstration) is deposited on a substrate and this initial layer is then patterned with metal islands, in the same or

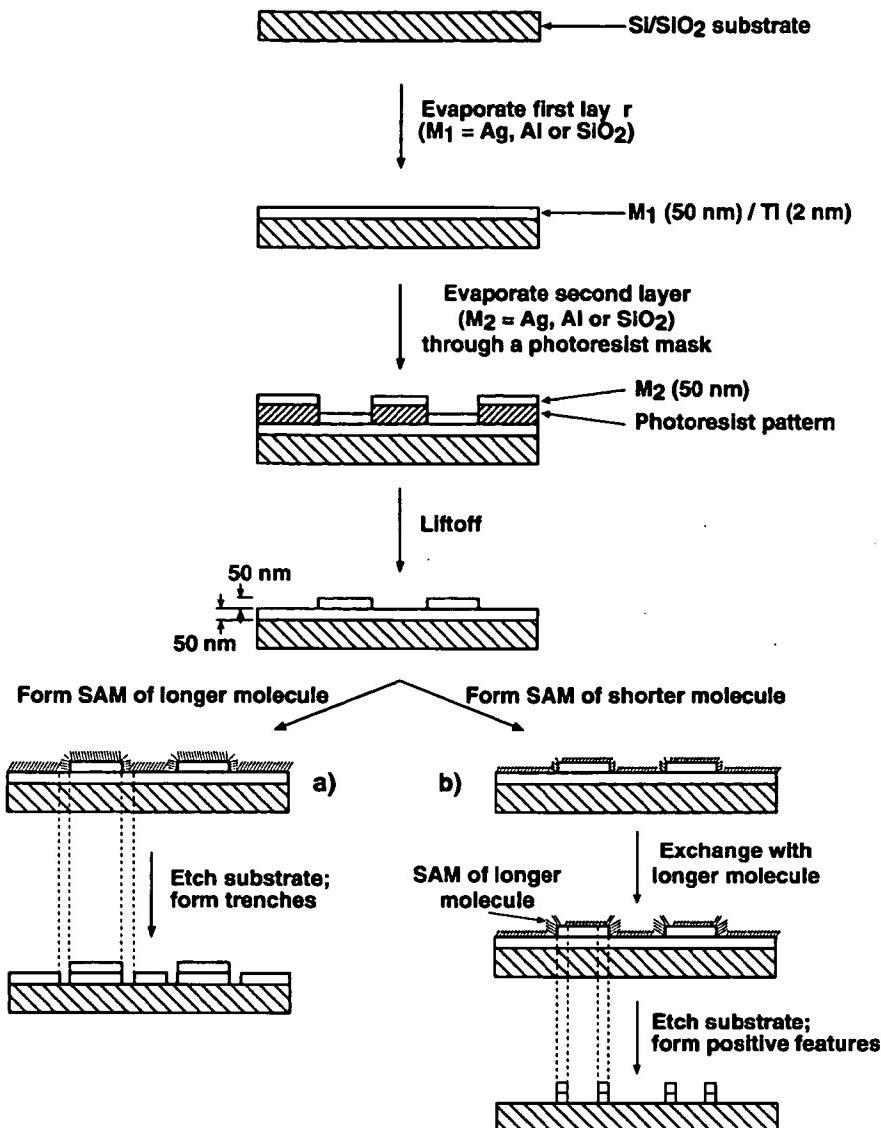


Figure 9. Schematic description of topographically directed etching.²⁰⁵

a different metal, by lift-off or a through-mask deposition. Exposure of the topographically patterned metal layer to a thiol generates a SAM that is disordered at the edges of the metal islands. The disordered regions etch selectively; the resulting features are the outline of the patterned island. The size of the etched region is controlled by the etching time; trenches obtained by a 10-s etch are ~50-nm wide (Figure 10). Exchange in the disordered region with a thiol of a longer chain length followed by etching gives the inverse pattern as the area with shorter chain thiols are etched first.

4.7. Lithography with Neutral Metastable Atoms

The development of optics for neutral atomic beams^{206–208} has enabled lithography to be carried out with an alternative exposure source—neutral metastable atoms.^{209,210} The use of neutral atoms offers two advantages relative to methods based on high-energy electrons or ions: (i) neutral atoms with low kinetic energies cause less damage to the mask than do high-energy charged particles; (ii) neutral atoms do not interact (over typical distances) electrostatically,

and (iii) electrostatic interactions do not limit the resolution. The use of patterned beams of neutral metastable atoms was originally demonstrated with SAMs of alkanethiolates on gold²⁰⁹ and later extended to other systems.^{210,211} In patterning SAMs on gold, the substrate is exposed to a beam of neutral metastable atoms (Ar^* or Cs^*) through a physical mask that is usually placed on the surface of the substrate.^{74,75,209} The release of energy from the metastable atoms induces sufficient damage to the unmasked areas of the monolayer to make them susceptible to etching. As a result, the gold under the damaged SAM can be removed by a wet etchant.

The electronic energy released from the neutral metastable atoms can also be used to decompose hydrocarbon vapors and deposit an etch-resistant carbonaceous film of unknown composition on the exposed regions of the surface (a form of so-called “contamination lithography”).^{77,210} Figure 11 shows SEM images of nanostructures that have been fabricated by lithography with neutral metastable atoms. The smallest structures that have been fabricated are arrays of holes in gold that are ~70 nm in

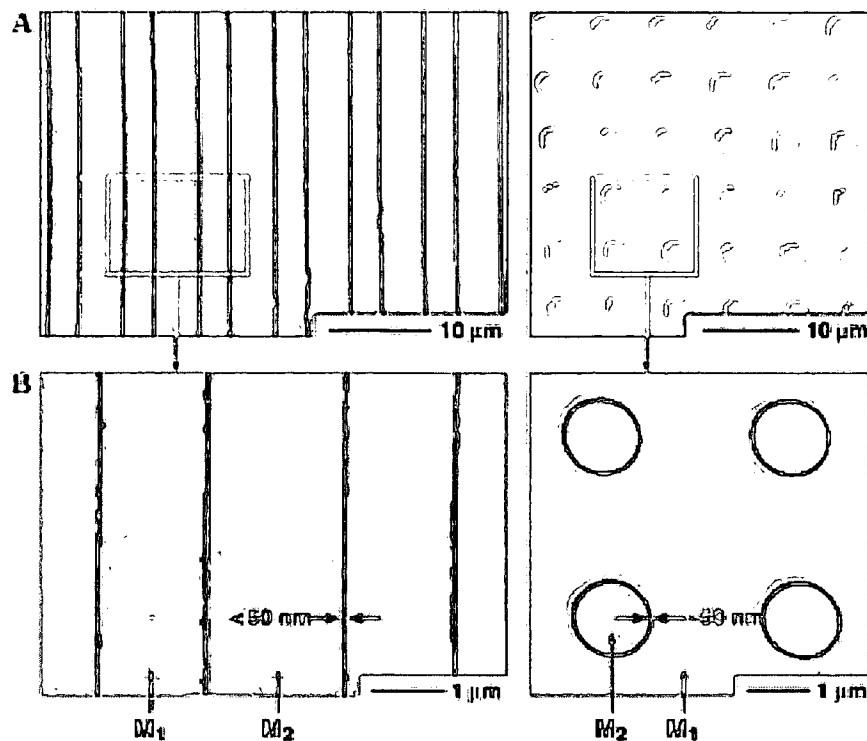


Figure 10. SEM images of nanostructures fabricated by topographically directed etching.²⁰⁵ Selective etching of the micropatterned substrates—2 μm wide lines (left) and a square array of circles with 1.5 μm diameter (right)—fabricated by depositing silver (50 nm) on an silver film through a layer of patterned photoresist, followed by lift-off. (A) Low-magnification SEM, showing the homogeneity of the pattern. (B) Trenches (\sim 50-nm wide) in the metal substrates fabricated by etching for 10 s. Reprinted by permission from *Nature* 1998, 394, 868–871. Copyright 1998, Macmillan Magazines Ltd.

lateral dimensions.⁷⁴ A disadvantage of the use of proximal stencil masks is that 1:1 imaging is required (for example, a 10-nm line requires a 10-nm slit) and small gaps are necessary (a <5 - μm gap is required for <7 -nm features) to prevent diffraction. Methods that rely on light to quench parts of a neutral metastable beam and those that use optical interference patterns for lenses to guide deposition of atoms on surfaces have the drawback that the densities of the features that can be formed in a single step are limited by the optical wavelength (unless, of course, the pattern of light is modulated during an exposure). Neutral-atom lithography will probably require development of appropriate stencil masks or projection optics before it becomes a practically attractive method; the use of optical forces provides a promising approach for constructing the atom optical elements that may be necessary.^{77,212}

4.8. Approaches to Size Reduction

A number of strategies are capable of reducing the feature size of a test pattern from 1 to 10 μm to \leq 200 nm. Tonucci et al. have fabricated glass membranes with hexagonal arrays of channels as small as \sim 30 nm in diameter by repeatedly drawing a bundle of glass fibers (consisting of an etchable glass core surrounded by a sheath of a different, etch-resistant glass) with a starting diameter of >1 μm .¹²² The nanochannel membrane fabricated from the cross section of the bundle can be further used as a mask in metal evaporation or as a mold in replica molding to fabricate nanostructure of other materials.²¹³ Birks et al. have fabricated photonic band-gap optical fibers

using a similar procedure.¹²³ Xia et al. have generated structures of 100–200 nm in size by mechanically manipulating the elastomeric stamp (or mold) used in microcontact printing or replica molding.^{124,126,127} Figure 12 shows a typical example in which the feature size has been reduced from \sim 2 μm to \sim 200 nm by two cycles of replica molding of polyurethane against a mechanically compressed PDMS mold. Other approaches relying on size reduction from an original pattern have also been explored as potential routes to nanostructures, including μ CP with controlled reactive spreading (Figure 5A)¹⁹¹ and μ CP or photolithography with a PDMS block cast from V-shaped microtrenches etched in a Si(100) substrate.^{125,128} Although these methods may lack the characteristics required for registration in device fabrication, they offer an easy access to simple patterns of nanostructures that are directly useful in making sensors, arrays of nanoelectrodes, and diffraction gratings.

5. Techniques for Making Regular or Simple Patterns

A number of techniques (Table 4) have been demonstrated for making regular or simple patterns of nanostructures such as parallel lines and arrays of holes or posts. These simple structures can be directly used as diffraction gratings, arrays of nanoelectrodes, and arrays of quantum dots. These techniques may also be valuable when combined with other more general techniques for pattern formation.

Interference or Holographic Lithography. The interference pattern generated by two mutually

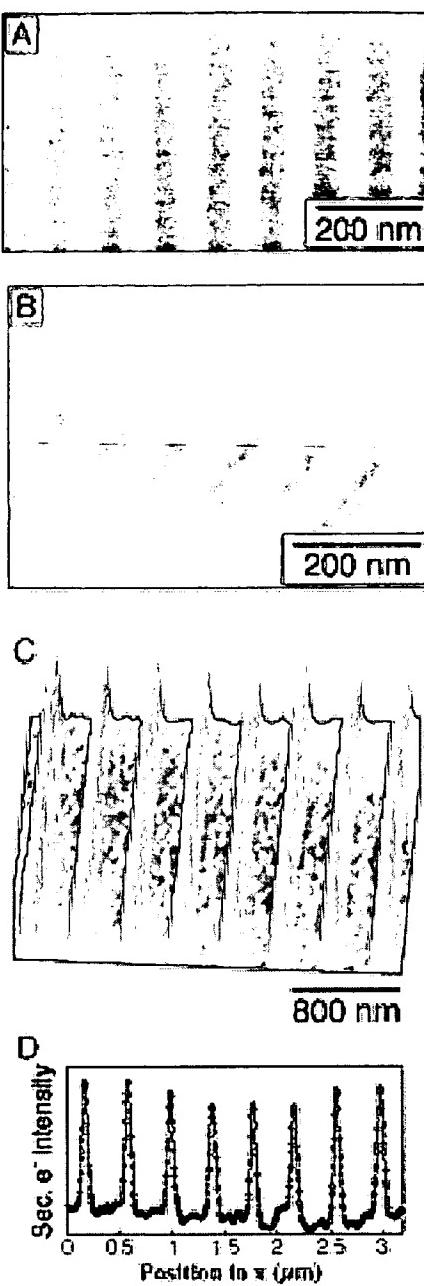


Figure 11. Patterned nanostructures fabricated by metastable atom lithography (courtesy of Prof. Mara Prentiss of Harvard University).^{74–77} (A) SEM image of features (white) etched in Si(110) by RIE. Features were patterned by contamination lithography using metastable argon atoms passed through a Si₃N₄ mask in contact with the surface. (B) Features viewed at a 75° angle; they have an aspect ratio greater than 2:1. (C) AFM image of the pattern etched into a Si(110) substrate. Features were patterned using metastable argon atoms passing through a standing wave. They are 12-nm tall and extended over an area of ~0.5 mm². (D) Average line profiles of SEM images used to determine the width of the features. Analysis of the secondary electron intensity versus position indicates that the FWHM of the lines is 65 ± 5 nm. A and B reprinted with permission from *J. Vac. Sci. Technol. B* 1998, 16, 1155–1160. Copyright 1998, American Vacuum Society.

coherent laser beams can be recorded in a thin film of photoresist.^{2,214–216} After development, an array of parallel lines is created in the resist film and the spacing between the lines is $\lambda/2n \sin(\theta/2)$, where λ is the wavelength of the laser, n is the refractive index

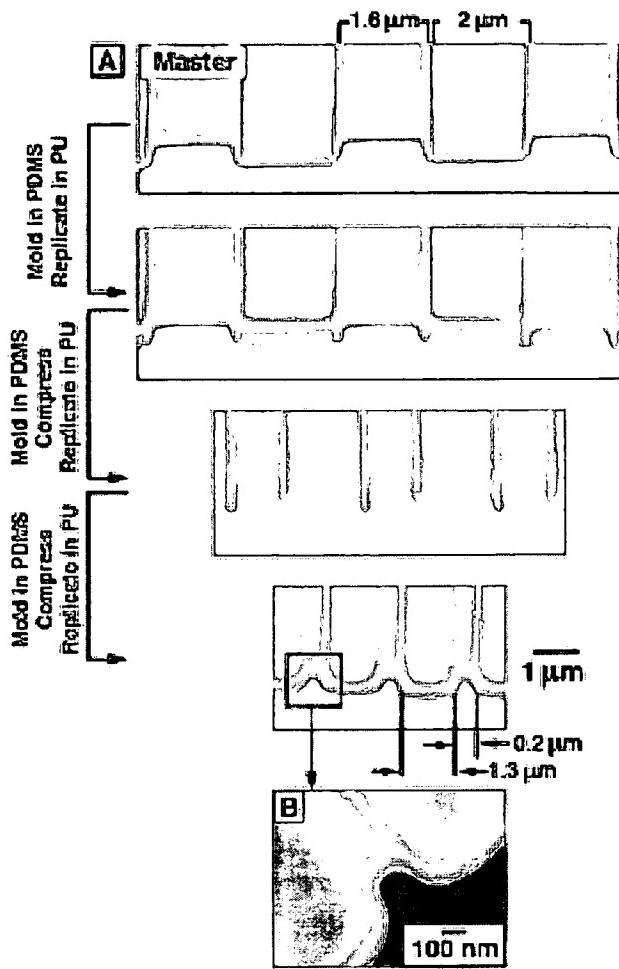


Figure 12. Cross-sectional SEMs of the original master (generated in a photoresist film coated on a silicon wafer using photolithography) and the polyurethane replicas generated after different cycles of replication in PDMS, compression, and replication in polyurethane.^{126,127}

of the photoresist, and θ is the angle of intersection of the beams. The pattern in the resist film can be further transferred into underlying substrates such as SiO₂, Si₃N₄, and silicon by RIE. This method is widely used in industry to manufacture holographic diffraction gratings and antireflection coatings. By exposure of the photoresist to the interference pattern twice (orthogonally to each other), 2-D arrays of posts can be fabricated,²¹⁷ and this procedure is a possible approach to manufacturing field-emission displays (FEDs).²¹⁸ Figure 13 shows the AFM image of an array of 200-nm posts in Si₃N₄ that was fabricated by holographic lithography using an argon-ion laser ($\lambda = 351$ nm), followed by RIE.²¹⁹

Complex patterns can be formed by intersecting more than two laser beams or by using multiple sequential exposures. The use of interference patterns produced through the use of multiple diffraction gratings^{220,221} increases the flexibility of holographic patterning. In these cases, the period of the holographically defined grating structure is equal to one-half of the period of a single diffraction grating divided by the number of gratings.²²¹ Gratings with periods as small as ~100 nm have been fabricated using this method. Imaging interferometric lithography uses multiple offset exposures or multiple

Table 4. Techniques for Making Regular or Simple Nanoscale Patterns^a

pattern formation using	writing	replication	refs
photons			
holographic lithography	yes	yes	214–221
deposition			
laser-focused deposition	yes	no	165, 223, 224
cleaved edge overgrowth	yes	no	113, 259, 260
self-assembly			
crystallization of proteins, colloids, and microspheres	yes	no	226–242
microphase separation of block copolymers	yes	no	106, 246–251
other			
anodic oxidation of aluminum	yes	no	252–257

^a In this table, yes means this technique is practical for writing or replication of features of ≤ 100 nm; no means this technique cannot practically be so used.

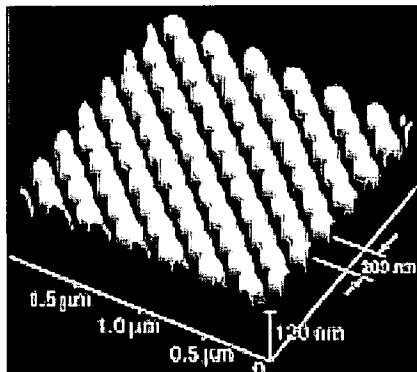


Figure 13. AFM image of Si_3N_4 nanostructures fabricated using holographic lithography,²¹⁹ followed by wet etching of photoresist and RIE of Si_3N_4 (the sample was provided by Prof. Henry Smith of MIT, and the AFM image was taken by Dr. Jabez McClelland of NIST).

mutually incoherent laser sources in a single exposure to generate interference and is theoretically able to achieve feature sizes of $\lambda/4$ while retaining the ability to make complex patterns.²²²

Laser-Focused Deposition. The interference pattern produced by the intersection of two or more laser beams can focus certain neutral atoms (for example, chromium or aluminum) into patterns as they deposit onto a surface.^{165,223,224} For two beams, counterpropagating parallel to the surface on which deposition occurs, each node of the optical standing wave acts as a cylindrical lens. Atoms passing through the standing wave are focused into a series of parallel lines (Figure 4A) with a period equal to half the wavelength of the laser. A two-dimensional standing wave formed by crossing more than two laser beams has been used to focus chromium or aluminum atoms into an array of posts on the surface of a substrate.²²⁵ Prentiss et al. have also used this technique to focus metastable Ar^* atoms that can be used for patterned deposition of ultrathin resists.⁷⁷

Crystallization of Proteins, Colloids, and Microspheres. Many methods are capable of forming two-dimensional crystals of spherical or quasi-spherical particles: proteins,^{102,226–231} colloidal particles,²³² and polymer latexes.^{106,233–237} The hexagonal-close-packed structures formed from spherical particles with diameters in the range of 300 nm to 4 μm have been used as physical masks, in conjunction with metal evaporation, to form patterned arrays of nanoscale metal islands.^{238–243} The lateral dimensions of metal islands and the spacing between them can be

precisely controlled by using spherical particles with different sizes. This method is remarkable for its simplicity and for its capability to form nanostructures over a wide range of sizes: the smallest spacing and pitch that have been attained simultaneously are ~ 50 and ~ 300 nm.²³⁶ New procedures that can produce defect-free 2-D crystals over relatively large areas are still needed. Nanostructures generated by current procedures may be useful, for example, in fabricating arrays of nanoelectrodes, quantum dot arrays, and photovoltaic cells. They may also find applications as photonic band-gap materials.²⁴⁴

Microphase Separation of Block Copolymers. Block copolymers having the correct dimensions for their blocks develop domain patterns at equilibrium: these patterns reflect the repulsions and attractions of the monomer units for one another and the constraints imposed by their covalent connections.^{100,101,245} For example, poly(styrene-*block*-isoprene), a block copolymer consisting of two chemically distinct ends, can exhibit a wide range of microphase-separated morphologies: spherical microdomains, cylindrical microdomains, and lamellar structures.^{246,247} The relative lengths of the two monomer units, their interactions with each other, and the character of the boundary surfaces primarily determine the geometry of the phase-separated state. The domains of block copolymer in a coated thin film can also be guided into arbitrary structures by patterning the surface of the substrate with monolayers with different interfacial energies.²⁴⁸ Because different monomers have different resistance to etching in RIE,¹⁰⁶ a spin-coated film of block polymer can be used as mask to transfer the domain pattern in the polymer film into the underlying substrate. Arrays of posts or holes with dimensions less than 20 nm have been successfully fabricated in Si_3N_4 using this procedure. The phase-separated polymers can also be used to guide the growth or deposition of materials such as gold.²⁴⁹ Means for controlling the geometry of the phase-separated patterns, such as those based on electric fields, for example, appear to be promising but will require further development.^{250,251}

Anodic Oxidation of Aluminum Films. Anodic oxidation of aluminum films in an acidic solution generates an array of hexagonally packed columnar holes in the film.²⁵² This procedure has long been applied in commercial production of alumina membranes used for separation. Pore densities as high as 10^{11} per cm^2 can be achieved. The size of pores can

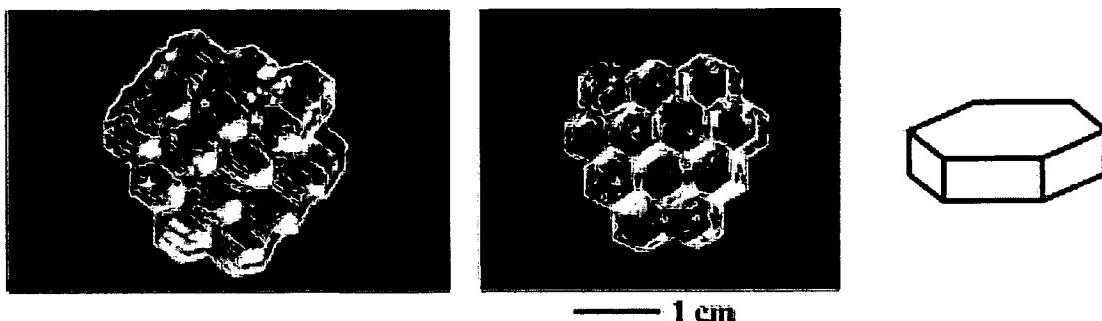
3D Self Assembly

Figure 14. Illustration of new concepts that are potentially useful in nanopatterning: meso-scale three-dimensional self-assembly of polyurethane plates,²⁶⁴ buckling of a PDMS surface patterned in bas relief with 600- μm circles,²⁶⁵ and a STM image (courtesy of Prof. Charles Lieber of Harvard University) of a single-walled carbon nanotube.²⁶⁶

be precisely controlled in the range of 5–200 nm by changing electrolyte composition, applied voltage, and temperature. A one-dimensional array of holes (with a high aspect ratio) was also fabricated by anodic oxidation of an evaporated thin film of aluminum sandwiched between two solid substrates.²⁵³ This kind of membrane has been extensively explored (largely by Martin and co-workers) as a template to synthesize nanostructures of a wide range of functional materials.^{89,254–257}

Cleaved Edge Overgrowth (CEO). As described previously in this review, CEO takes advantage of multilayer structures grown by molecular-beam epitaxy (MBE).^{113,258} It has been employed to fabricate atomically precise structures such as quantum wires and quantum dots. In this technique, a superlattice structure consisting, for example, of alternating layers of AlGaAs and GaAs is made by MBE.¹¹² The sample is then remounted in the growth chamber in an orthogonal direction to the original mounting and cleaved through the thickness of the multilayer structure *in situ* to produce an atomically clean surface. MBE or electrochemical deposition is then used to grow epitaxial layers on selected regions of the exposed surface. Conventional forms of lithography have also been used to pattern this cleaved surface. This approach enables the formation of intersecting quantum wells with atomic- or angstrom-level control of the thickness in two directions.²⁵⁸ Devices such as quantum wire lasers formed from

the intersection of ~7-nm wide quantum wells have been fabricated with this method.^{259,260} More recently, quantum dot structures have been formed at step edges on the cleaved surface of GaAs²⁶¹ and through a 2-fold cleaving method.²⁶² For the fabrication of many types of quantum structures, CEO yields more uniform structures than electron-beam or optical lithography or selective area deposition, because CEO incorporates the uniformity and precision of MBE.^{112,263} CEO is, however, limited to those structures that can be fabricated along the natural cleavage directions of a substrate and along lattice planes on which MBE growth occurs easily.¹¹³ Also, the structures must be built up from intersecting planes of material.

6. New Concepts, Not Yet Demonstrated for 100-nm-Scale Patterning

The challenges to generating broadly useful techniques for fabricating on nanometer length scales have led to the development of radically different approaches (Figure 14). Most of these methods have been developed at the μm or mm scale and need to be scaled down to the <100-nm scale. Some of them have been demonstrated for generating nanostructures but have not yet been adapted for patterning surfaces.

Meso-Scale Self-Assembly (MESA). The concepts of molecular self-assembly have been extended to the directed self-assembly of meso-scale (100 μm

to 5 mm sized) objects.^{104,264,267,268} The assembly of hexagonal PDMS plates at the water-perfluorodecalin (PFD) interface, driven by capillary forces, is an example.^{104,267} By controlling the hydrophilicity of the sides of these plates, they can be directed into arrays having a range of structures. MESA is able to generate a substantial range of structures and is a promising technique for precision microassembly.

Whether it will be practical to use capillary forces to assemble nanostructures is presently unclear. Nagayama has used capillary forces (at the receding edge of a meniscus) to assemble nanospheres;²³⁴ there is, therefore, some hope that these interactions might be useful (albeit in a different context than that used by Bowden et al.¹⁰⁴) in nanostructure assembly. Other forces have also been used to make regular assemblies of <100 nm-scale objects: the examples of Grier and Murray²³⁶—based on combinations of Coulombic interactions and more complex self-polarization—indicate that if capillary forces fail, it is possible to consider other types of interactions. The work of both Mirkin et al.²⁶⁹ and Alivisatos et al.,²⁷⁰ for example, show how DNA can be used to assemble arrays of gold colloids as small as a few nanometers. Other promising interactions that could be used to direct assembly of nanoparticles include magnetic and electrical fields: Ferrofluids and electrorheological fluids containing nanoscopic particles can be aligned into ordered structures in a magnetic²⁷¹ or electric field.²⁷² Both are currently being investigated in wide ranging applications: for example, ferrofluids have been shown to be useful in nanomotors and generators.²⁷³ A key, unsolved problem in this area is the development of flexible methods for making small (<100 nm) objects with a substantial degree of control over their shapes and the character of their individual faces.

Buckling. When a block of PDMS is heated, it expands. If the surface is heated briefly with an oxygen plasma (to introduce a thin SiO₂-like layer) or coated with a thin film of gold by e-beam evaporation and then allowed to cool, the difference in coefficients of thermal expansion of the bulk PDMS and the relatively incompressible surface layer places that layer under compressive stress.²⁶⁵ The stress is relieved by formation of uniform buckles in the surface. On a flat, uniform surface, these surface waves form highly irregular patterns. If, however, the PDMS surface is embossed, the bas-relief pattern causes ordering in the surface waves. Highly regular structures with periodicity of <1 μm have been produced.

The spontaneous formation of small ordered structures (the surface waves) under the influence of a larger template (the bas relief) is a process that could be useful if the period of the waves could be reduced by a factor of 10–100 from those observed in current examples. The phenomenon of spontaneous ordering through formation of surface waves has been analyzed theoretically, and the materials properties required to achieve waves with shorter wavelengths are understood.

Assembly Using Optical Tweezers. Forces generated by refraction of a tightly focused laser beam passing through an interface between two media with

different indices of refraction can be used to manipulate micrometer-sized particles and assemble them into 3-D arrays. Burns et al. used 1–5 laser beams passing through a glass sample cell to organize particles (with a range of compositions: polystyrene beads, titanium dioxide colloids, and biological cells) and generated what they termed “optical matter”: systems held together by the interaction of oscillating electromagnetic fields with matter, rather than by the Coulombic interactions of electrons with nuclei.²⁷⁴ The periodicities are governed by the wavelength of light used ($\lambda = 514$ nm) and the angle of the intersecting beams. This method of crystallizing particles is capable of generating complex (albeit periodic) patterns. It can also be used to hold particles in place while the liquid carrying the particles is cured into a solid, for example. Structures formed in this manner may be useful for three-dimensional photonic band-gap crystals.²⁴⁴ Optical tweezers have also been considered as a tool to assemble nanometer-scale parts or to make connections to self-assembled structures in a nanosystem.

Growth of Buckyballs and Nanotubes. New forms of carbon nanostructures—buckyballs and nanotubes^{266,275–277}—are an important new class of materials, in part because they can be either semiconductors or metallic conductors.^{266,277} They can also be converted into nanorods of other functional materials such as ceramics by reacting with different chemical reagents.²⁷⁸ In principle, single-wall, conductive graphitic nanotubes are probably nearly ideal quantum wires: they are environmentally stable, defect-free, and intrinsically conductive. Unfortunately, as-prepared carbon nanotubes are usually tangled mats, and although it is now possible to cut them, separate them, and manipulate them individually, it is presently difficult to envision making large, ordered, connected structures with them.²⁷⁹ The future application of carbon nanotubes in practical device fabrication will probably depend on the invention of some new way of growing them (or equivalent structures) in the desired patterns.²⁸⁰ Although buckyballs have been assembled into a nanometer-sized abacus on a copper substrate using an STM tip, carbon nanotubes will probably be more useful than buckyballs in fabrication of nanodevices.²⁸¹

7. Conclusions

Physics and electrical engineering now depend on the fabrication of structures with dimensions less than 100 nm to generate tools and devices for many areas of research. Materials science, chemistry, and biology are beginning to require similar capabilities in fabrication. Research in all of these fields will advance the fundamental understanding of systems with dimensions less than 100 nm; it will also create new technologies to support commercial applications of nanoscopic structures.

The largest, most obvious, but not necessarily most realizable opportunities for nanostructures are in electronics, where smaller sizes have historically allowed the production of denser, faster circuits and where the ability to produce nanostructures may lead to new types of devices that operate on quantum

mechanical principles. For true nanosized devices, however, serious problems in circuit design will have to be solved before complex, high-speed integrated circuits can be fabricated. The problem is not just a problem in fabrication of individual small-scale devices; the interactions between these devices, the dissipation of the heat that they generate, and the design of circuits incorporating large numbers of devices differing significantly and unavoidably in their performance are all problems that will also have to be managed.

Examples of applications for nanostructures in areas outside of electronics may include, for instance, ultrasmall mechanical and chemical sensors based on nanoelectromechanical systems and nanoelectrodes, optical elements with nanometer dimensions for photonic band-gap structures or near-field storage devices, and structures for use in cell biology that will have the ability to sense and manipulate phenomena that occur at scales smaller than organelles. These applications, together with a fundamental interest in nanoscience, provide compelling motivation for research into techniques for nanofabrication.

We divide the task of fabricating complex nanostructures into four parts: (i) preparing the masters; (ii) replicating these masters into patterns of sacrificial or functional materials; (iii) transferring the replicated patterns of sacrificial materials into patterns of functional materials; and (iv) registering and aligning patterns to existing features. Conventional scanning electron-beam lithography is now the most widely used technique for generating the masters used in microelectronics (that is, the first task). Although there are certainly opportunities for improving this technique and for establishing other methods that have similar or superior capabilities, we believe that electron-beam lithography, in basically its current form, can provide an acceptable solution to generating masters with feature sizes less than 50 nm and that it will remain an indispensable tool for this purpose. We also believe that the third task—transforming structural into functional patterns—represents a relatively minor challenge for most applications, since many of the established methods—lift-off, patterned etching or ion implantation, and shadowed evaporation—do not depend strongly on feature size. Although registration (the fourth task) is a significant challenge, its solution will likely rely on clever engineering rather than on new chemistry or chemical methods (although self-assembly may ultimately make self-registration possible in some systems).

Rapid, reliable replication of features near or below ~ 100 nm, on the other hand, is currently both a significantly unsolved problem and one in which we believe innovation in chemical and physical methods can introduce fundamentally new techniques. It seems likely that whatever technologies are used for fabrication in the region below 100 nm will not represent simple engineering extensions of conventional photolithography, although sophisticated enhancements may play a role. There may exist, therefore, an opportunity to introduce new ideas in replication of micro- and nanostructures that is unique in the

50-year history of this field of technology. This review has focused, therefore, mainly on techniques for replication of master structures having nanoscale features into sacrificial or functional materials.

Characteristics present in an ideal method for replication would include low operating and capital cost, flexibility in the materials that can be used, fidelity in the replication, ability to pattern on nonplanar surfaces, low density of defects, high speed and parallel operation, and capability for fabrication in three dimensions. Because all of these characteristics may never be present in a single method, it may be necessary to combine techniques in ways that exploit their various advantages and to design strategies for fabrication that use different methods for different parts of the structure.

Historically, photolithography has been the dominant technique for replication since the origin of fabrication of microelectronic systems; it satisfies many of these requirements, and it has been used for every generation of technology in microelectronics. Photolithography will probably continue to provide an attractive solution to replication at scales down to, perhaps, 70 nm by using 193 nm (or 157 nm) light and/or performance-enhancing techniques such as phase-shifting masks, off-axis illumination, optical proximity correction, or photoresists based on top surface imaging with silylation and dry development. Several companies in the microelectronics industry can now fabricate working devices such as microprocessors and memory cells with features as small as 80 nm using deep uv (248, 193 nm) photolithography, phase shifting masks, and optical proximity correction.²⁸⁶ Projection photolithography using transmission optics seems, however, to be reaching a point—set by the physics of diffraction and the properties of materials—where it may no longer be the most effective method of fabricating small structures. Lithographic methods based on proximity mode exposure with X-rays and projection systems that use EUV radiation, electrons, or ions are now being aggressively developed for replication at resolutions (<100 nm) that are very challenging to achieve with conventional projection-mode photolithography. These techniques are currently in an engineering development phase; each already has the demonstrated capability to replicate patterns with features less than 100 nm over large areas in a parallel fashion. Although it is not yet clear which of these techniques (if any) will ultimately emerge as an acceptable approach, projection electron-beam lithography, in particular, appears to be promising because (i) it relies on electrons, whose usefulness in generating masters with features well below 100 nm is inarguable, and (ii) it uses projection optics, which allows features in the replicas to be much smaller (~ 4 times) than those on the mask.

This review focused on a number of exploratory techniques for replication of masters based on high-resolution printing, embossing, molding, and conformal near-field optics; it also touched on other techniques, including replication using arrays of scanning probes or beams of neutral atoms and topographically directed etching and photolithography. Approaches

based on physical contact, such as the soft lithographic techniques, are particularly attractive because they circumvent limitations due to diffraction, allow patterning on curved surfaces, and allow patterning a wide range of materials and materials precursors. These capabilities, which are absent from many other methods, have already enabled soft lithography to begin to establish niche applications in fabricating microfluidic analytical systems,^{282,283} in constructing new types of active fiber-optic devices that use microstructures printed onto the surface of the fiber,²⁸⁴ and in patterning surfaces presenting complex organic functional groups that direct the attachment and metabolism of mammalian cells.^{6,7,285} Demonstrating direct compatibility with materials commonly used in microelectronics, controlling registration and distortion, and reducing the density of defects are areas in which all of these methods require further development before they can be competitive with the much more highly developed processes of conventional microelectronics.

Our experiences with soft lithography suggest that traditional metrics, such as feature size and distortion, have only limited value when applied to new techniques with unfamiliar characteristics that do not conform to these metrics. In fact, many future opportunities for microfabrication may exist not only in the development of fabrication techniques that improve speed, resolution, and distortions and in those that enable new processes such as purely additive fabrication of all-organic devices but also in the design of systems that have fundamentally new structures and capabilities (for example, 3-D memories and junctions between biological and electronic components).

Finally, we also included in this review several methods for fabrication of patterned structures based on self-assembly, templated growth, and size reduction that have only been demonstrated at sizes much larger than those of central concern in micro- and nanofabrication. We believe that these (and doubtless many other approaches) are promising directions for exploratory research in fabrication and precision assembly and that they embody new science that may develop into fundamentally new approaches to fabrication of small, patterned structures. In their current state of development, these techniques are potentially valuable only in niche applications or in those where they can be naturally integrated with other more general fabrication techniques, but their fundamental limits and their futures have not been defined. As with soft lithography, however, some of these techniques allow patterning of unconventional materials into structures that can be difficult or impossible to achieve with any standard approaches.

The rich range of technical opportunities in micro- and nanofabrication and the number of new approaches to small-scale fabrication combine to suggest a future where control of structure and function can be accomplished with a sophistication that we cannot presently imagine. The range of these new approaches is now making it possible for makers and users of very small structures to move beyond the familiar question, How can one use photoresist and

silicon to make useful structures?, to a newer question, Since it is possible to pattern many materials into many geometries with <100 nm features, what new structures can we now make and what new functions can we now achieve?

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9. References

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